Summer 1993

Hydrogeochemical Interactions in a Subalpine Watershed, Mount Baker National Recreation Area, Washington

JoAnn Michele Holloway
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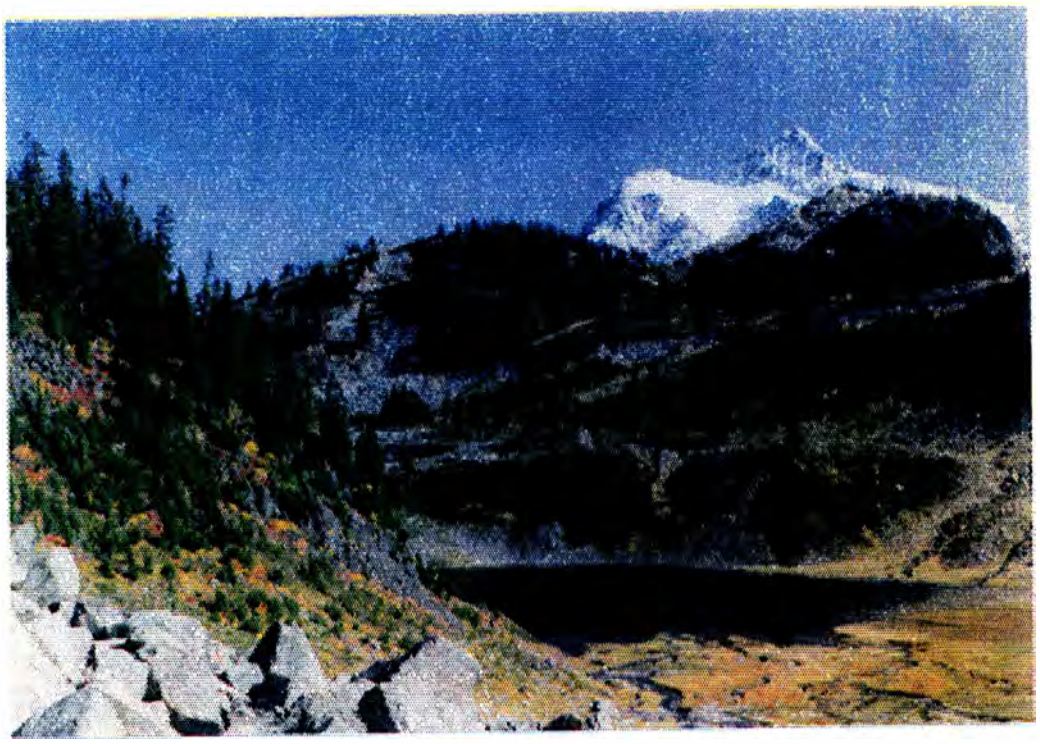

In the beginning there were rocks
and it was good.
After that the rains came,
and then there were lakes.

Hydrogeochemical Interactions in a Subalpine Watershed, Mount Baker National Recreation Area, Washington

by

JoAnn Michele Holloway

Accepted in Partial Completion
of the Requirements for the Degree of
Master of Science

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Hydrogeochemical Interactions in a Subalpine Watershed, Mount Baker National Recreation Area, Washington

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A Thesis Presented to
The Faculty of
Western Washington University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

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by
JoAnn Michele Holloway
July, 1993

MASTER'S THESIS

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ABSTRACT

The Upper Bagley watershed was monitored from April to November, 1992. The watershed is described as a series of chemically distinct subsystems: 1) the snowpack, 2) soil solutions, and 3) surface water. The hydrogeochemical interactions between these subsystems were investigated in the Upper Bagley watershed. Chemical analyses of these fluids were used to identify how soil solutions vary from water derived from the snowpack and what impact soil solutions have on surface-water chemistry.

Water-ice interactions alter the snowpack chemistry, enriching the melt in calcium, magnesium, sodium, chloride, and sulfate that accumulate at the surface of ice crystals. The melt from the Upper Bagley watershed is enriched in calcium and sodium by a factor of three and in magnesium by a factor of six relative to snow concentrations. Chloride and sulfate concentrations are up to four times greater in the melt fraction. Nitrate does not become concentrated in the melt fraction since the equilibrium of nitrate in the snowpack is controlled in part by denitrification.

Soils in the Upper Bagley watershed are Entisols, or primitive soils. Two soils types were defined on the basis of clay content and the ability of the soil to support vegetation. Soil I, a clay loam that originates from glacial till and volcanic ash, is composed of montmorillonite, inorganic colloids, and organic acids. This soil supports vegetation dominated by heather and sedge. Soil II, a gravely sand loam derived from andesite with sparse vegetation, is primarily andesine and inorganic colloids. Pore fluids from these soils are chemically distinct. Pore fluids from Soil I (Pore Fluid I) have greater ion concentrations that those from Soil II (Pore Fluid II). Pore Fluid I is dominated by calcium and sulfate and is more acidic than Pore Fluid II, which is dominated by sodium.

The chemical composition of surface water in the Upper Bagley watershed reflects the mixing of fluids derived from snow and soil solutions. End-Member Mixing Analysis suggests that solutions from the inlet, outlet, and lake are a mixing product between four end-members: 1) the relatively dilute snow and melt, 2) surface water that has leached cations from vegetation, 3) Pore Fluid I, and 4) Pore Fluid II. When plotted against chloride concentrations, calcium, magnesium, and sulfate provide evidence for the mixing of fluids in the Upper Bagley watershed. Processes other than simple mixing also influence the chemistry of the Upper Bagley watershed. Nitrate and alkalinity concentrations for the fluids do not provide evidence for interaction between fluids. The equilibria of these ions are more strongly affected by biological transformations (nitrate) and gas exchange with the atmosphere (alkalinity).

Normalized mixing analysis was used to indicate individual sample clusters that do not demonstrate simple mixing. Ions were normalized for chloride and plotted against each other. Plots of calcium, magnesium, and sulfate normalized to chloride are strongly linear because the equilibria of these ions are controlled in part by mixing. Correlation of the data clusters that diverge from the linear plot pattern with field conditions at the time of collection indicates that redox reactions and aerosol deposition also control the chemical equilibria of the watershed.

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ACKNOWLEDGEMENTS

I first wish to thank my committee members, Scott Babcock, Chris Suczek and Robin Matthews. I appreciate your understanding as I showered you with a barrage of last-minute thesis drafts. Thanks also to Chris Suczek for being a friend as well as Department Chair. George Mustoe has been an unofficial committee member, providing technical advice and constructing field toys (ahem, equipment) for me.

Tom Storch of the Huxley College of Environmental Studies took time to discuss wild interpretations I had for some of my data. Liz Schermer's input inspired deeper thought on my part, resulting in a new and improved thesis. Bill Wilson of the Department of Chemistry helped set up my analytic procedure for water samples. Clint Burgess and Terry Meredith of the University Instrument Center provided me with lessons in analytic chemistry. Geoff Landis and Jim Mullen in the Science Shops built my snow-corer and helped make my soil columns for my lab experiments. Jim Johnston of the Washington Department of Wildlife provided physiographic data on Upper Bagley Lake.

Fellow students have helped in various capacities. Bo Bergquist introduced me to Upper Bagley Lake as a possible field area. Kris Alvarez, Robin Buchan, Ingrid Hutter, Duane Olson, and Brian Sandidge braved sunburns, blizzards, and icy waters to assist me in the field. I hope the picas, marmots, eagles, herons, and huckleberries were just compensation. Craig Cooper came to my rescue when I needed to use a laser printer and when I needed to laugh. Many encouraging conversations geological and otherwise were had with Melanie Carpenter. David Haasl was a great source of encouragement in the latter stages of this production.

A special thanks goes to Frank Miyazaki for letting me live in his beautiful house in Bellingham for an incredibly reasonable rent. Kris Alvarez has been a wonderful roomate for the last year-and-a-half. The tea breaks with lengthy discussions, moments of bizarre humor, tasty breads, and unexpected presents at unpredictable times have been great.

Colin Zelt made it possible for me to purchase the computer on which this thesis was written and subsidized some fine vacations. His e-mail messages have been an inspiration. Harold and Jo-Ann Zelt provided a pleasant vacation spot on Vancouver Island during my stay in the region. My aunt, Judy Vitzthum, provided me with food and a place to stay in Seattle, not to mention a splendid Easter basket.

Finally, I would like to thank my mother, Jan Hebert, for her early financial planning and her encouragement that made it possible for me to attend graduate school. I am also grateful for my childhood introduction to the natural world that would lead to my pursuit of geology and watershed hydrology. Thanks Mom!

This research was supported in part by a Summer Field Research Grant provided by the Department of Geology, Western Washington University.

I. INTRODUCTION

The purpose of this study is to investigate the interactions between snowpack, soil solutions, and surface water in the Upper Bagley watershed, a subalpine watershed in the North Cascades. The chemistry of these fluids will be used to evaluate their relationship. The primary goals are 1) to identify how soil solutions vary from water derived from the snowpack and 2) determine what impact soil solutions have on surface water chemistry.

Studies conducted on small watersheds are effective in determining the interactions that occur within a watershed system. The physical, chemical, and biological parameters are more easily constrained in a system that is limited in area. Typically, the hydrology, geochemistry, and vegetation of an ecosystem are studied over a number of years. Long-term biogeochemical studies on small watersheds have been conducted at Birkenes, Norway (Mulder et al., 1990; Christophersen & Neal, 1990; Müller et al., 1993), in the Hubbard Brook Experimental Forest in New York State (Likens et al., 1977), in the Loch Vale watershed in Colorado (Baron, 1992), and in other areas in North America and Europe.

The Upper Bagley basin has been monitored over a limited time period and so provides an incomplete a body of information upon which to base a geochemical mass balance. A watershed is variable annually as well as seasonally. The monitoring of Upper Bagley basin was performed during 1992, a year with below-normal precipitation during which the ablation of the permanent snowpacks exceded the accumulation of snow. The results of this investigation should be considered with this in mind.

Study Area

The Upper Bagley Lake watershed was selected for this study because it is accessible year around and data for it are available from previous studies (Loranger, 1986; Bergquist, 1991). Upper Bagley Lake is located in the Mount Baker National Recreation Area in northwest Washington (Figure 1). The watershed is 2.17 km^2 in area. The lake is at an elevation of 1800 m and occupies a cirque.

The bedrock in the watershed consists of recent andesite flows from Mount Baker on the south side and Permian Chilliwack greenstone to the north (Figure 2). The geology in Figure 2 is based on aerial photos and was checked in the field. Soils in the watershed have been mapped as shallow alpine meadow soil derived from bedrock, Mesozoic extrusive igneous rock, and Recent andesite (Mount Baker National Forest, 1970). Approximately thirty percent of the drainage area is covered by vegetation, primarily heather, huckleberry, partridgefoot, and sedge. Mountain hemlock grows in less than five percent of the drainage area (Johnston, 1993), mainly along the higher slopes in the drainage.

Neoglacial studies in the Mount Baker area indicate that glacial advances occurred in the area 2800 to 2600 years before present, 800 years ago, 400 years ago, and into the twentieth century (Fuller, 1980; Burke, 1972; Harper, 1992). Thin soil coverage, less than a meter thick throughout the basin, and sparse vegetation suggest a recent glaciation. There is a marked difference between soil profiles within the watershed and those just outside of the basin. Soils in the Upper Bagley basin are shallow, less than 20 cm in depth, and exhibit no clear development of soil horizons. Soils along the banks of Bagley Creek are up to two meters thick and have well developed horizons.

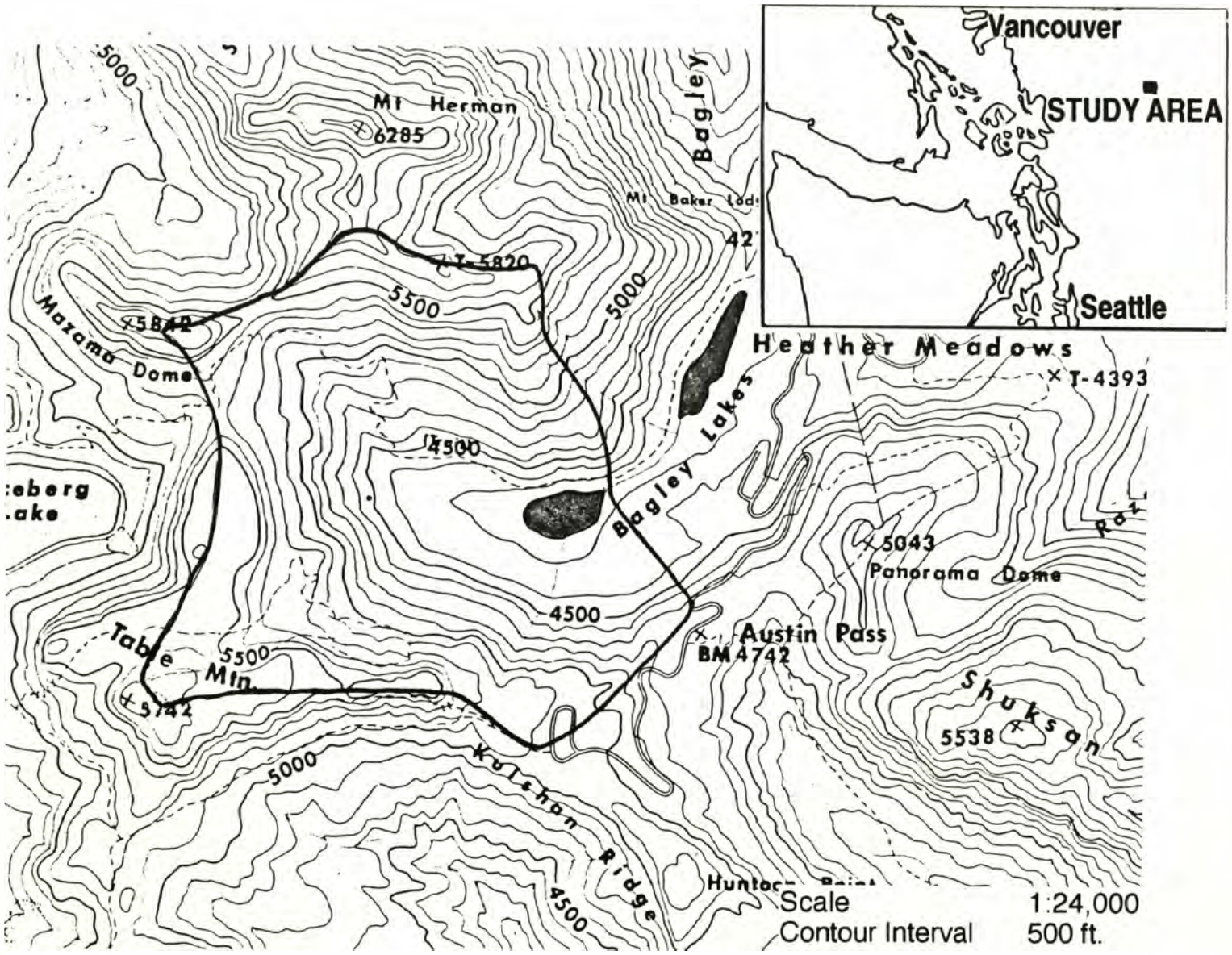


Figure 1. Location map for the Upper Bagley watershed. The heavy black line marks the watershed boundary.

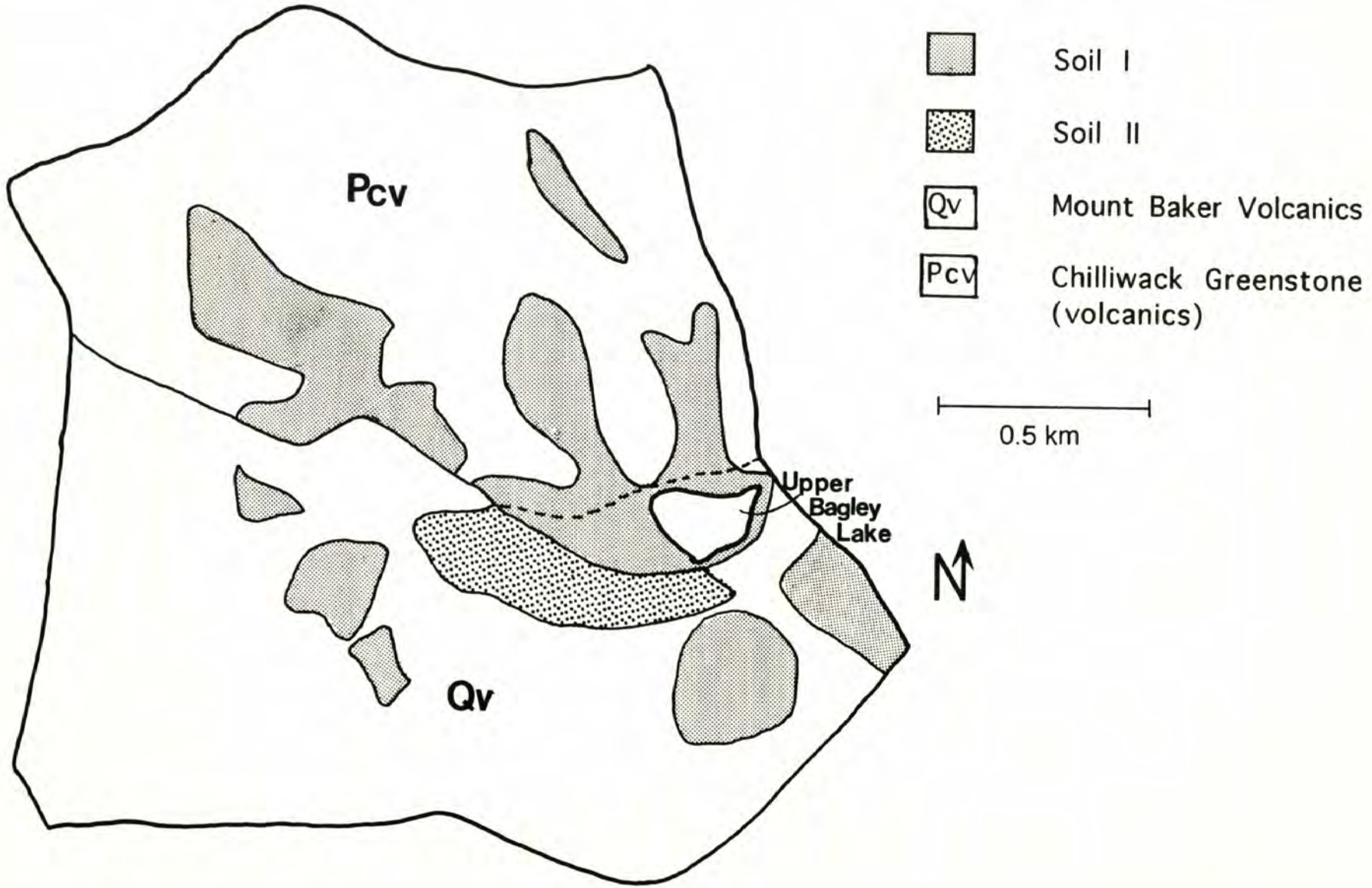


Figure 2: Soils and bedrock of the Upper Bagley watershed.

Upper Bagley Lake has a surface area of 34.4 m^2 and a maximum depth of 6.4 m (Johnston, 1993). The ratio of watershed area to lake area is 63 (Johnston, 1993). Surface water enters Upper Bagley Lake through a braided stream that flows in from the west and as unchannelized overland flow. Subsurface water enters the lake as baseflow and groundwater. The outlet, Bagley Creek, drains to the west into Lower Bagley Lake, an artificial water body created by a concrete dam in 1927 (Neff, 1991).

Previous Work

Watersheds in the North Cascades are susceptible to acidification by pollutants generated in the Puget Lowland. Laird et al. (1986) collected snowpack samples for chemical analysis from the Cascades and the Sierra Nevada every 25 km from the Canadian-U.S. border. The samples from the North Cascades show increased concentrations of NO_3^- and $SO_4^=$ with decreased NH_4^+. This trend is attributed to the transport of airborne pollutants from the Seattle/Tacoma metropolitan area and from Mount St. Helens.

Based on the assumption that carbonation reactions are the predominant chemical weathering mode operating in the North Cascades, acid neutralization capacity (ANC) was used as an indicator of total weathering products in solution for a series of studies on North Cascade lakes (Brakke & Loranger, 1985; Loranger et al., 1986; Loranger, 1986; Bergquist, 1991). The assumption of the importance of carbonation reactions in this region is erroneous. Hydrolysis reactions are a more significant weathering mode in the North Cascades, because carbonate rocks are infrequent in the region. Nevertheless, ANC is a valuable assessment of the relative concentrations of weathering products in solution.

A survey of sixty watersheds in the North Cascades (Brakke & Loranger, 1985), found that most lakes in this region have a low ANC. Acid neutralization capacity is roughly equivalent to alkalinity. For the lakes investigated, 68 percent had an ANC less than 200 μeq/l and 37 percent were below 100 μeq/l ANC. Upper Bagley Lake had an ANC of less than 200 μeq/l . The ANC dynamics were further investigated in five of these lakes, including Upper Bagley Lake (Loranger et al., 1986). The ANC was depressed to 70 μeq/l in Upper Bagley Lake during spring snowmelt and increased over the fall and winter to a peak of 146 μeq/l in April, 1985, just prior to snowmelt (Loranger, 1986). The year to year variability of ANC in the snowpack and lakes was found to be insignificant.

Loranger (1986) monitored lake and snowpack chemistry of Upper Bagley and five other North Cascade watersheds from 1984 to 1985. Surface nitrate and sulfate levels in all six lakes were at a maximum during snowmelt in April and May. Over 75 percent of the nitrate equivalency was attributed to the snowpack by comparing the concentration of nitrate in the lakewater to that of the snowpack. Snowpack contribution to sulfate in Upper Bagley lake was estimated at 31 percent (Loranger, 1986). These estimates suggest that the snowpack is a major source of nitrate and sulfate, usually associated with anthropogenic sources, to the Upper Bagley watershed.

Calcium was found to be the dominant cation found in the snowpack in the Bagley Lake watershed, followed by sodium, magnesium, and potassium (Loranger & Brakke, 1988). Depth profiles for Upper Bagley Lake indicated complete chemical mixing of the lake, promoted by the shallow depth and large watershed-to-lake ratio (Loranger & Brakke, 1988).

Bergquist (1991) monitored the chemistry of the outlet and snowpack in the Upper Bagley watershed from June, 1989, to September, 1990. Lake ANC

was diluted from 110 μeq/l to 85 μeq/l during snowmelt. Initial results from Bergquist's study indicated that ANC is reduced during spring snowmelt and during periods of high rainfall. Low soil-moisture conditions in late summer and early fall resulted in an increase in ANC. Concentrations of nitrate and sulfate decreased in the snowpack as the snowmelt season progressed, suggesting that these anions are concentrated in melt-water from the snow. There was a peak in nitrate in the lake that corresponded with peak snowmelt, providing further evidence that the snowpack is a significant contributer of nitrate to the Upper Bagley watershed.

Cation exchange capacity (CEC) was measured for three soils from the Upper Bagley watershed (Bergquist, 1991). The soils were described on the basis of the surrounding vegetation and were not distinguished on the basis of physical characteristics. Soil samples were collected in a forested area, in huckleberry and heather, and in sparse heather and mosses. The CEC for the soils was low, varying from 0.07 to 9.99 μeq/l. The CEC was greatest in the soil from the forested area and the lowest in the soil collected in heather and mosses. Bergquist (1991) concluded that if the Upper Bagley watershed were impacted by acid rain generated in the Puget Lowlands, it would take a relatively short time for aluminum to become mobilized from the soils.

This study adds to previous work in the Upper Bagley watershed by investigating the effect soil solutions have on the surface water chemistry. Soil pore waters have been found to be significant in the storage and release of chemical constituents into the watershed (Christophersen and Neal, 1990; Robson et al., 1993). An understanding of the interaction between soil solutions and surface waters in this relatively pristine drainage basin will provide a better understanding of how anthropogenic pollutants impact other drainages.

II. METHODS

Field Sampling

In order to evaluate the effect of soil solutions on surface water chemistry, the chemical composition of snow, surface water, and pore fluids was determined. Snow in the Upper Bagley watershed occurs as seasonal snowpack and in permanent snowfields. Both occurrences were sampled. In addition, the melt-water from a permanent snowfield was analyzed to determine the changes that occur in the solution chemistry as the snow melts. Surface water collected includes the inlet, outlet, and Upper Bagley Lake. Two sites described later in this chapter were selected for the extraction of soil pore fluids.

Water and snow samples were collected in the Upper Bagley Lake basin eleven times between April and November, 1992. The sampling schedule is given in Appendix 1. Samples were collected every two weeks during the growing season and monthly for the rest of the period. The growing season is the period from late June to late August when the snowpack in the basin has melted and perennial vegetation is active.

Bottles, bags, and sampling devices were washed in 1 N HCl prior to sample collection. The sample containers and lysimeter were soaked in deionized water for two days after being washed in acid. The snow corer was rinsed eight times in deionized water.

Water samples were collected from the outlet of Upper Bagley Lake throughout the period of study. The samples were selected to monitor changes in surface water, snowpack, and soil solution chemistry. The inlet, a braided stream, was sampled from the largest channel during the growing season to assess input into the lake. An outlet sample was collected at the confluence of Upper Bagley Lake and Bagley Creek. The outlet sample provided a measure

of output from the drainage basin as well as an approximation of lake chemistry. Samples were taken from three sites on Upper Bagley Lake to ensure that the outlet sample provided a reasonable approximation of lake chemistry. Surface water was collected in the middle of the lake and from the east and west ends when the lake was free of ice.

Sediment samples were collected from Upper Bagley Lake three times over the course of the summer. Lake water that had been in direct contact with these sediments was analyzed to assess the contribution of sediments to the chemical composition of the waterbody.

Snow samples were collected to determine atmospheric input into the drainage basin. The snowpack was sampled at depth in April and May using a stainless steel corer with a Teflon plunger. The snowpack profile samples were sealed in doubled plastic bags, and the melt water was transferred to bottles in the lab. Snow samples were named using the depth at which the snow core was taken (i.e. Snow 0 for surface, Snow 2 for a sample taken at 2 m). Snow was collected during the remainder of the study from a permanent snowfield located on the southwest slope of the watershed. The surface layer of snow was removed to provide a fresh surface, and the sample was scraped into a plastic bottle. Melt-water was collected by allowing the water to drip directly from the snowfield into the sample container. This sample was passed through a 0.45 μm filter in the field to remove rock and plant debris.

Two major soil types, Soil I and Soil II, were defined on the basis of clay content and the ability of the soil to support vegetation. The characteristics of these soils are summarized in Appendix 2. Soil I, a clay loam, is an Aquent that originates from glacial till and volcanic ash. This soil supports vegetation dominated by huckleberry, heather, and sedge. Soil II, a gravely sandy loam, is a Psamment derived from andesite with sparse vegetation. Pore fluids were

collected from the type localities of these soils, designated as PI and PII, respectively (Figure 3). PI lies to the northwest of Upper Bagley Lake. PII is on the southwest side of the lake. Both sample sites are located approximately 50 m above the elevation of Upper Bagley. Stream samples were collected adjacent to PI (Stream I). One stream sample was collected adjacent to PII (Stream II). It was not possible to collect pore fluids from Soil II after late July as surface runoff at this location was negligible. Soil pore fluids were collected *in situ* using a portable lysimeter consisting of an aluminum oxide extraction filter attached to a lucite barrel (Figure 4). Pore fluids were sampled by establishing a vacuum inside the lysimeter with a hand pump. At each site the lysimeter was washed with deionized water and rinsed with a small amount of sample fluid before collection of the sample.

Leaching Experiments

An experiment was set up for this study to determine how readily ions are leached from soils by water. The lower halves of two lucite columns were loosely packed with soils from PI and PII, and deionized water was added to the upper part of the column. The two columns were stored at a constant temperature of 5 °C. The first water sample was taken seven days after the columns were established to allow silt and clay-sized particles to settle out. The water was sampled 1.5 cm above the water-soil interface every 7 days for a month.

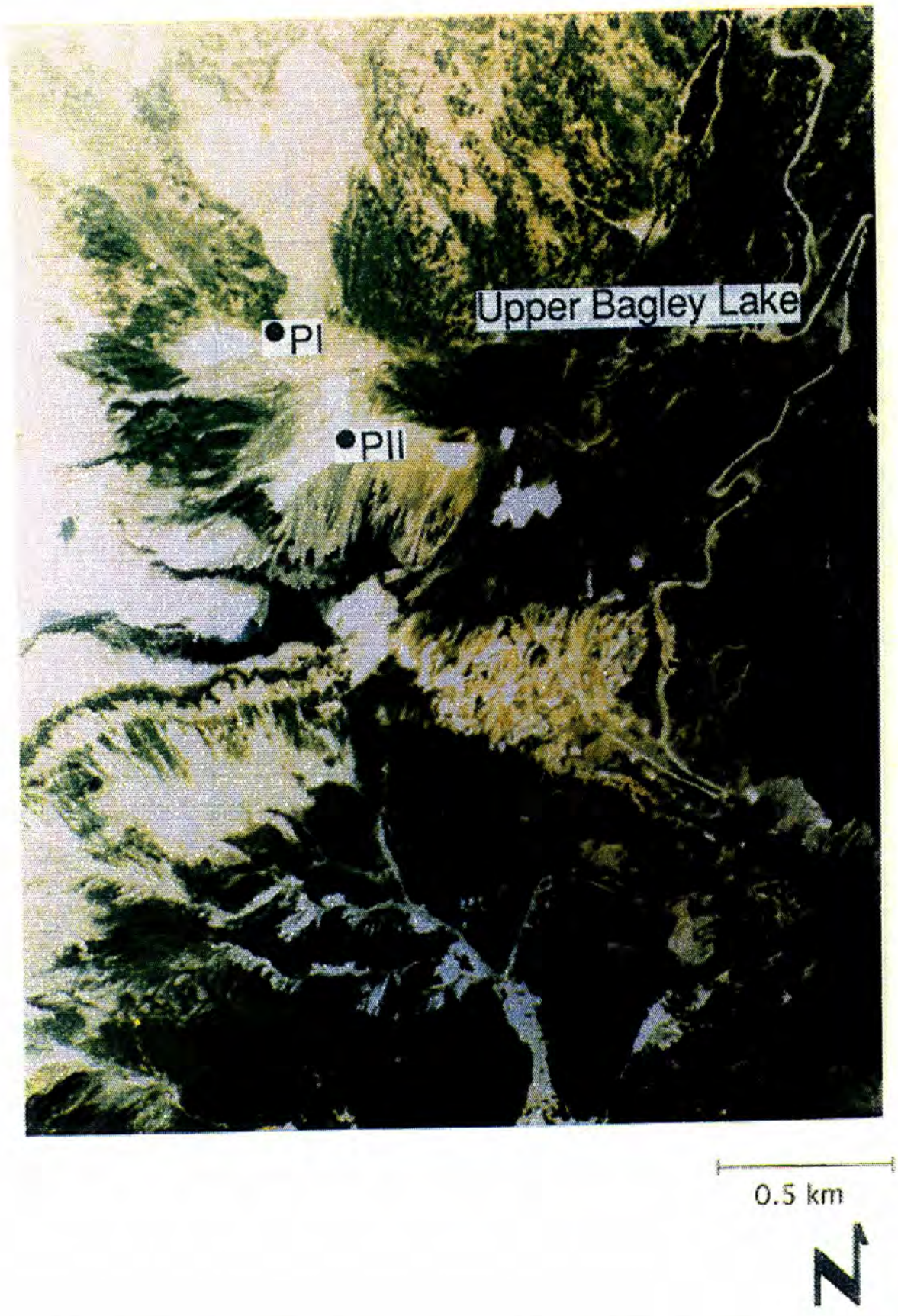


Figure 3: Aerial photograph showing sample locations for pore fluids. The photo was taken in August, 1991.

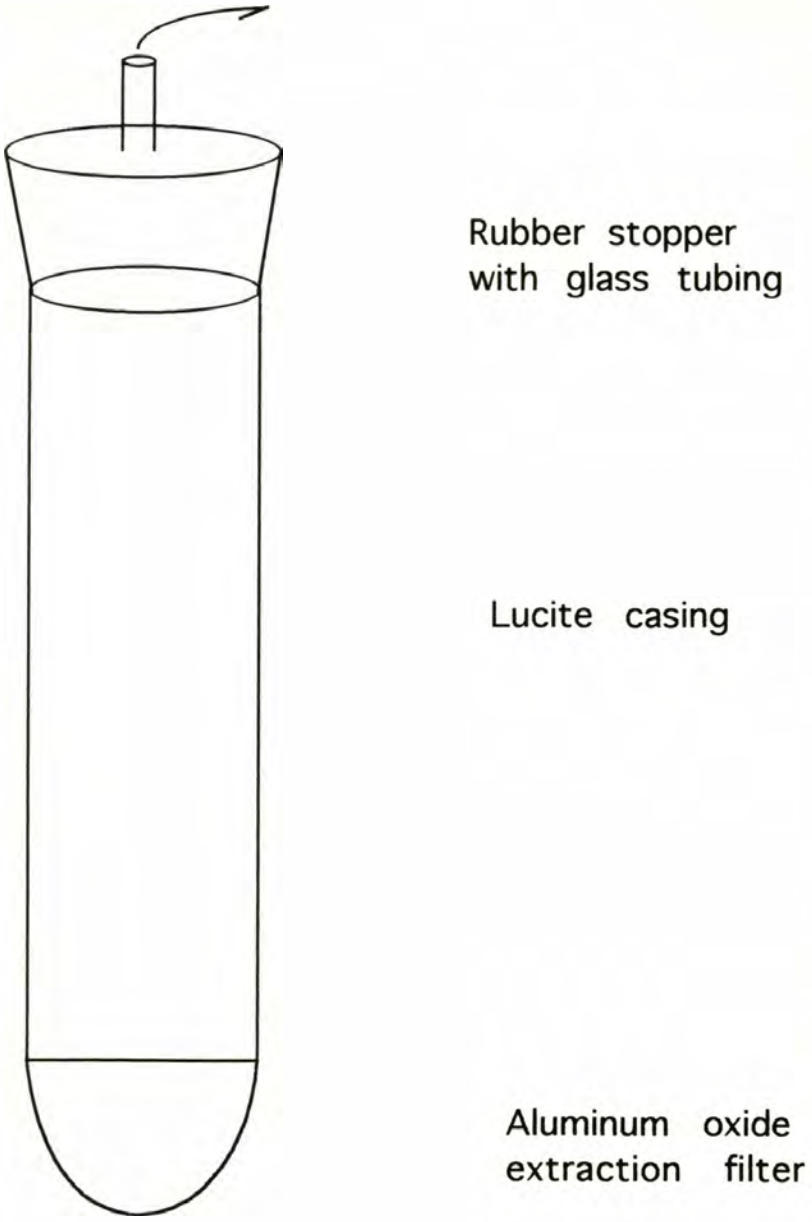


Figure 4: Portable lysimeter used to collect soil solutions. Suction is established using a hand-pump.

In another experiment, deionized water containing vegetation from the Heather Meadows area was allowed to sit at 5 °C for a week to determine the effect of decaying plant material on water chemistry. Heather and sedge were the plants selected for this experiment as they are the predominant vegetation type in the Upper Bagley watershed.

Chemical Analyses

Calcium, magnesium, sodium, and potassium were analyzed by flame atomic absorption spectroscopy using a Perkin Elmer 306 spectrophotometer. Chloride, nitrate, and sulfate were measured on a Dionex Model 2010i ion chromatograph with a fiber suppressor. Samples analyzed for anions were filtered through a 0.25 μm filter during injection into the ion chromatograph. The analytical methods and detection limits for these analyses are given in Table 1. Detection limits are based on the lowest measurable concentration of each ion as determined using standard solutions.

Calcium carbonate alkalinity was determined within 24 hours of sample collection using a Gran plot (Stumm & Morgan, 1981). Titrants used were 0.01 N HCl and 0.16 N H_2SO_4. The titrants were standardized using sodium bicarbonate.

Field pH was measured using a Markson digital pH meter and a Cole-Parmer pH probe. A Markson digital pH meter was used during the first six sampling dates. Values for the two meters agreed within 0.1 pH units. The meter was calibrated in the field using buffers at pH 4 and 7. Laboratory pH was determined under quiescent conditions using a Markson digital pH meter. Samples were allowed to equilibrate to buffer temperature, approximately 20 °C, before measurement in the laboratory.

Table 1: Methods of Analysis

Parameter	Instrumentation	Method	Det. Limit
Alkalinity	Markson pH meter	Gran Plot [1]	
Calcium	Flame AAS	EPA 215.1[2]	0.02 mg/l
Chloride	Ion Chromatograph	EPA 300.0	0.02 mg/l
Magnesium	Flame AAS	EPA 242.1	0.01 mg/l
Nitrate	Ion Chromatograph	EPA 300.0	0.01 mg/l
Potassium	Flame AAS	EPA 258.1	0.02 mg/l
pH	Markson pH meter Cole-Parmer pH probe	EPA 150.1	
Sodium	Ion Chromatograph	EPA 273.1	0.02 mg/l
Sulfate	Ion Chromatograph	EPA 300.0	0.01 mg/l

[1] Gran plot from "Aquatic Chemistry, 2nd ed." (Stumm & Morgan, 1981)

[2] EPA methods from "Methods for Chemical Analyses of Water and Wastes (U.S. EPA, 1983).

Soil Mineralogy

Soil samples from sites PI and PII were collected and air dried for laboratory analysis. The clay mineralogy of the soils was determined using an x-ray diffractometer. Rock fragments and plant debris were removed by passing the sample through a 200-mesh sieve. The sample was then disaggregated using a mortar and pestel and transferred to centrifuge tubes. Samples were centrifuged for four minutes at 1000 RPM to allow all grains larger than 2 μm to settle. A two percent sodium carbonate-sodium bicarbonate solution with a pH

of 9.5 was added to some samples to remove organic matter. Both treated and untreated samples were mounted for x-ray diffraction analyses. Glycerol was added to powder samples for x-ray diffraction to differentiate between vermiculite and montmorillonite (Whittig, 1965).

III. RESULTS

Quality Assurance

Data for field samples are given in Appendix 2. The standard deviation for chemical data was estimated from duplicate measurements as described by Arbogast (1990) using Equation 1:

$$S_d = (\Sigma R^2 / 2k)^{1/2}; \quad (1)$$

where R is the difference between two duplicate measurements and k is the total number of paired data used. Analytical error was determined from the standard deviation for laboratory duplicates. For every 12 samples analyzed, a sample or standard was selected and analyzed a second time. The standard deviation between duplicate samples collected in the field result from sample handling and also reflect the chemical inhomogeneity inherent to watersheds. The standard deviations from all duplicate samples are shown in Table 2.

Table 2: Standard Error and Confidence Intervals*

	Laboratory Duplicates		Field Duplicates		
	Sd	k	Sd	k	μ
Ca	0.04	10	0.06	8	+/-0.04
Mg	0.01	10	0.05	8	+/-0.03
Na	0.01	10	0.01	8	+/-0.01
K	0.03	10	0.01	8	+/-0.02
Cl	0.01	10	0.03	8	+/-0.02
NO_3	0.01	10	0.01	8	+/-0.01
SO_4	0.01	10	0.07	8	+/-0.04
ALK			0.05	5	+/-0.04

* Standard deviation (S_d) and confidence intervals (μ) are in mg/l.

Confidence intervals were calculated from the larger standard deviation for each ion as:

$$\mu = {}^{+/-} tS_d / (k)^{1/2} \qquad (2)$$

where t is Student's t with a 95 percent probability level.

The pH of water samples is inconsistent between field and laboratory measurements, in part because the surface of a sample is in continuous equilibrium with the atmosphere. Bringing a water sample from a high elevation to near sea level will expose the sample to varying concentrations of atmospheric CO_2. The pH is controlled by the equilibrium:

$$H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow CO_2 \qquad (3)$$

Field pH was taken as a control for this variation. The standard deviation between field and laboratory pH for 43 sets of paired data is 0.60 pH units. The confidence interval based on this standard deviation for pH is +/- 0.16 pH units. The inconsistencies in field and laboratory pH are the result of sample handling and uncontrolled conditions in the field. Samples equilibrate under laboratory conditions or become contaminated in sample containers, altering the pH. The pH measurements taken in the field are made inaccurate by standardizing the pH probe with a buffer solution that has not equilibrated with the temperature of surface water from various locations. Lakes, streams, and soil solutions are open systems relative to hydrogen ions. Fluctuations of tenths of a pH unit will occur while a measurement is being taken, causing uncertainty. Diurnal cycles of photosynthesis and respiration for various organisms will result in a significant variation of pH at different times of day in the same location (Wetzel, 1983). In spite of the various sources of uncertainty described, pH is still a useful evaluation of ion activity in water. Relative changes in pH provide information about overall changes in a water-body. Some samples collected for this study were rejected on the basis of pH. A water sample with a pH of less

than 5.5 was considered to be contaminated during sample handling. Laboratory pH is used in this study as it was measured in a controlled environment and was more consistently measured than in the field.

Hydrology

Horton overland flow comprises a large proportion of flow into Upper Bagley Lake when there is heavy precipitation. As observed in the field, most of the runoff during a storm is unchannelized. The predominance of Horton overland flow during a storm is due to the steep slopes of the drainage basin and the limited soil cover. Just under 30 percent of the surface of the Upper Bagley watershed is covered by soils.

Geochemical data collected in a watershed vary as a function of discharge. Streams in the Upper Bagley watershed are ungauged, and establishing a permanent gauging station as part of this study was not feasible. In the absence of stream-discharge data, two methods were used to account for the effect of dilution on water chemistry: 1) precipitation data were used to provide a relative measure of dilution in the Upper Bagley watershed, and 2) water chemistry data were corrected for chloride, considered to be a conservative ion (Mulder et al., 1990). A conservative ion is chemically inert, not being significantly depleted or increased in concentration relative to a constant volume of water through inorganic equilibria or through biologically mediated reactions. Assuming that chloride is a conservative ion implies that there are no long-term sources or sinks of chloride into the biota. Fluxes in chloride are assumed to be in response to changes in discharge, with soil and lake sediment acting as a sink for chloride during periods of low discharge and as a source during periods of high discharge. Based on this assumption, dividing ion concentrations by chloride concentrations measured for the same

sample corrects for fluctuations in discharge. Data for the inlet, outlet, lake, and pore fluids were corrected for dilution using chloride. Data from the snowpack and snowfield were not corrected for chloride because fluctuations in surface-water discharge do not directly effect snow chemistry.

Precipitation and temperature data were collected by the U.S. Forest Service at a remote automated weather station established near Kidney Creek at an elevation of 914 m. Although this station is located at a lower elevation than the Upper Bagley Lake watershed, the precipitation recorded at 914 m will be proportional to that falling at 1800 m. Rasmussen & Tangborn (1976) found that runoff from high elevations in the North Cascades can be estimated with reasonable accuracy based on data from lower elevations. Precipitation data for Kidney Creek are shown in Figure 5.

Water Chemistry

Snow Profile

Depth profile samples were collected from the snowpack from the surface to the maximum depth of the snow in April and May, 1992. The pH for the snowpack at depth is shown in Figure 6. Snow samples are vulnerable to pH changes from the field to the laboratory. The original snow consists of ice crystals derived from cloud water. Cloud water pH is as low as 3 in Western Washington (Basabe et al., 1989). The surface of the ice crystals react with the atmosphere at Upper Bagley watershed, increasing the pH on the outer crystal. When the snow melts, the surface area of the sample that can react with the atmosphere increases, and the pH will again be effected. The pH of a snow

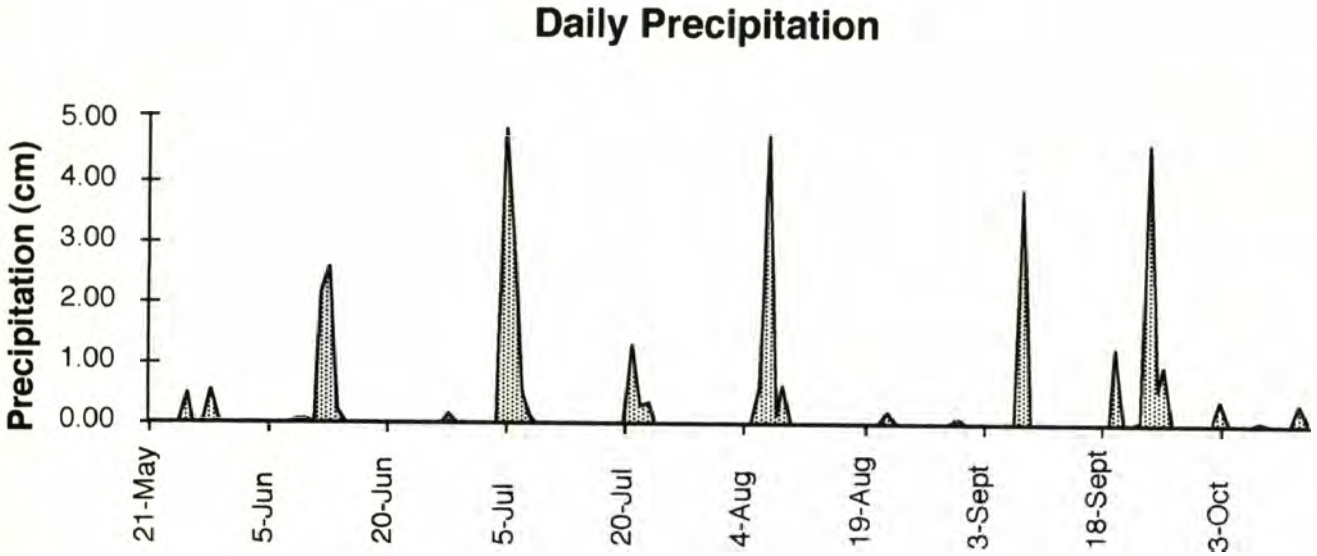


Figure 5: Precipitation data measured at Kidney Creek, 1992.

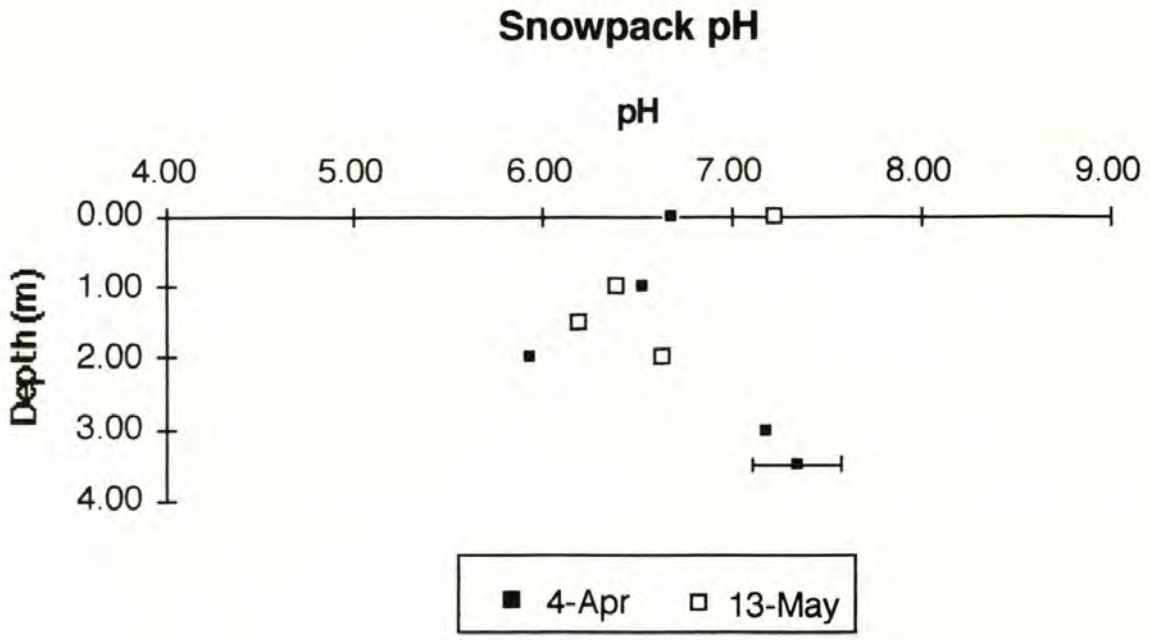


Figure 6: Snowpack profile showing pH for April and May, 1992. The confidence interval is shown for the April sample taken at 3.5 m.

sample collected, therefore, does not indicate the actual snow pH, but gives an approximation of what happens to the snow *in situ*.

The pH of the snowpack samples are between 6.5 and 7.5 at the surface where the snow is newly fallen. The pH decreases with depth until 1.5 to 2 m below the surface, after which it rises again. This pattern reflects chemical changes that happen during snowmelt. These changes are explained Chapter IV.

Sulfate and nitrate are in the greatest concentrations in the fresh snow at the surface of the snowpack in April (Figure 7A). There is a positive inflection for sulfate and chloride in April and May at a depth of 1.5 to 2 m, where the negative inflection for pH occurs. Alkalinity in April declines at 2 m, where pH also declines (Figure 7). In April and May, sodium and potassium peak at a

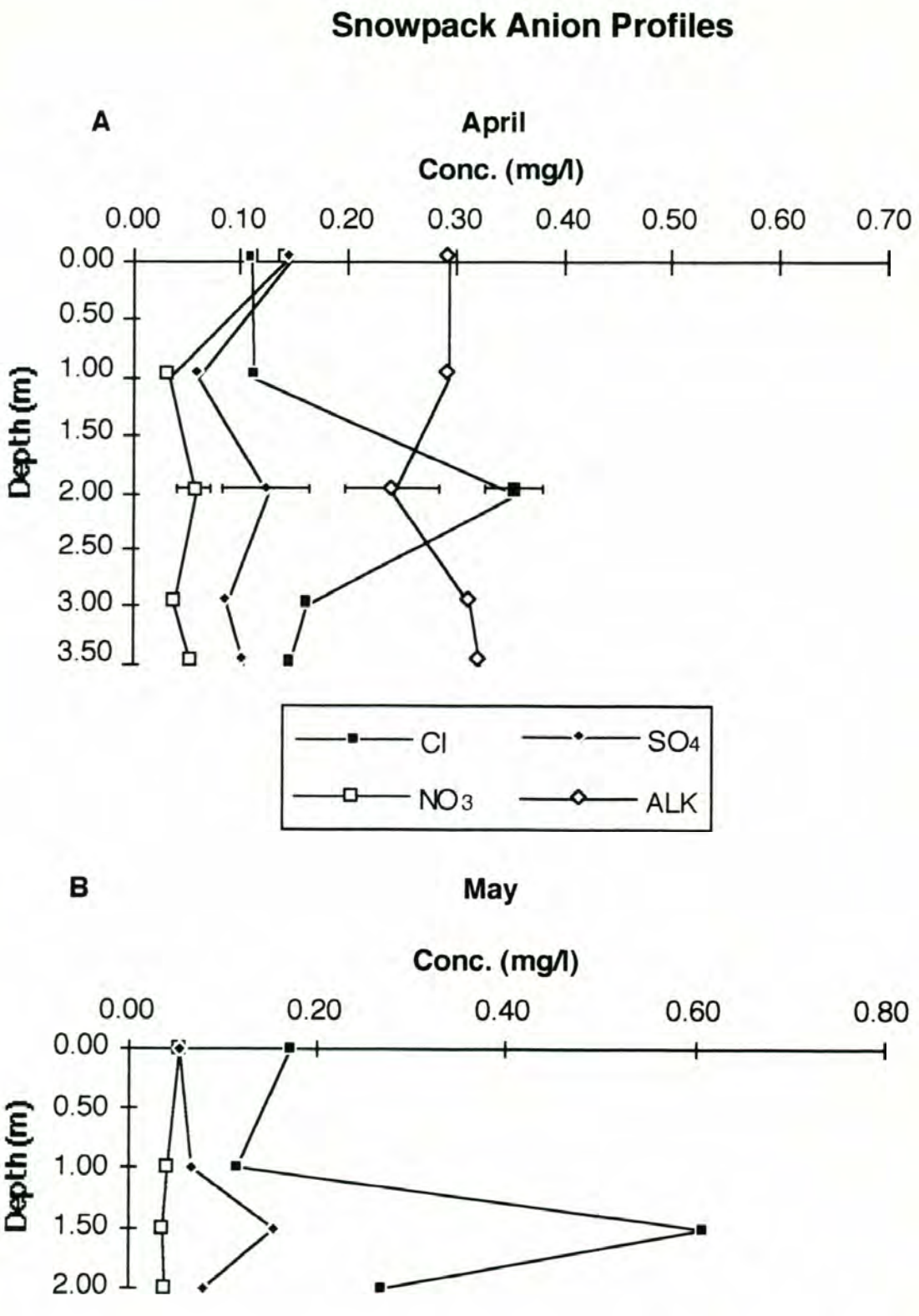


Figure 7: Snowpack profile showing anions for April (A) and May (B), 1992. Confidence intervals are shown for the data points from April at 2 m. Alkalinity was not measured for the May samples.

depth of 1.5 to 2 m, where the inflection point for pH occurs. Magnesium increases at depth but doesn't have a peak concentration at a specific depth (Figure 8). The increase in sulfate, nitrate, sodium, and calcium, and hydrogeat the same depth is related to the interaction between snow and melt where melt-water is enriched in some ions (See Chapter IV).

Snowfield

Samples were collected from a permanent snowfield in the southwest end of the watershed during the summer of 1992. The pH of snow from the snowfield increases slightly over the course of the summer with a pH of nearly 8 in October (Figure 9A). Alkalinity increases through the season after early July (Figure 9B). The decline in alkalinity from late June to early July is due to dilution by precipitation from major storm that occurred on July 5. A storm that occurred on August 6 may have caused the decline in alkalinity between August 2 and August 16.

The concentrations of all major ions peak on July 20 (Figure 10A). The enrichment of the snowpack in these ions may be caused by a period of rapid melting following the July 5 storm. The melt fraction tends to have higher concentrations of major cations and anions than the snow it originates from (Figure10B).

Pore Fluids

The two pore fluids that were collected are chemically distinct, reflecting the different mineralogies of the soils described in a later section. Pore Fluid I is more acidic than Pore Fluid II (Figure 11) and has higher concentrations of most major ions, especially calcium (Figure 12). Figure 13A, which has not been corrected for chloride, more clearly shows the potassium trend in Pore Fluid I.

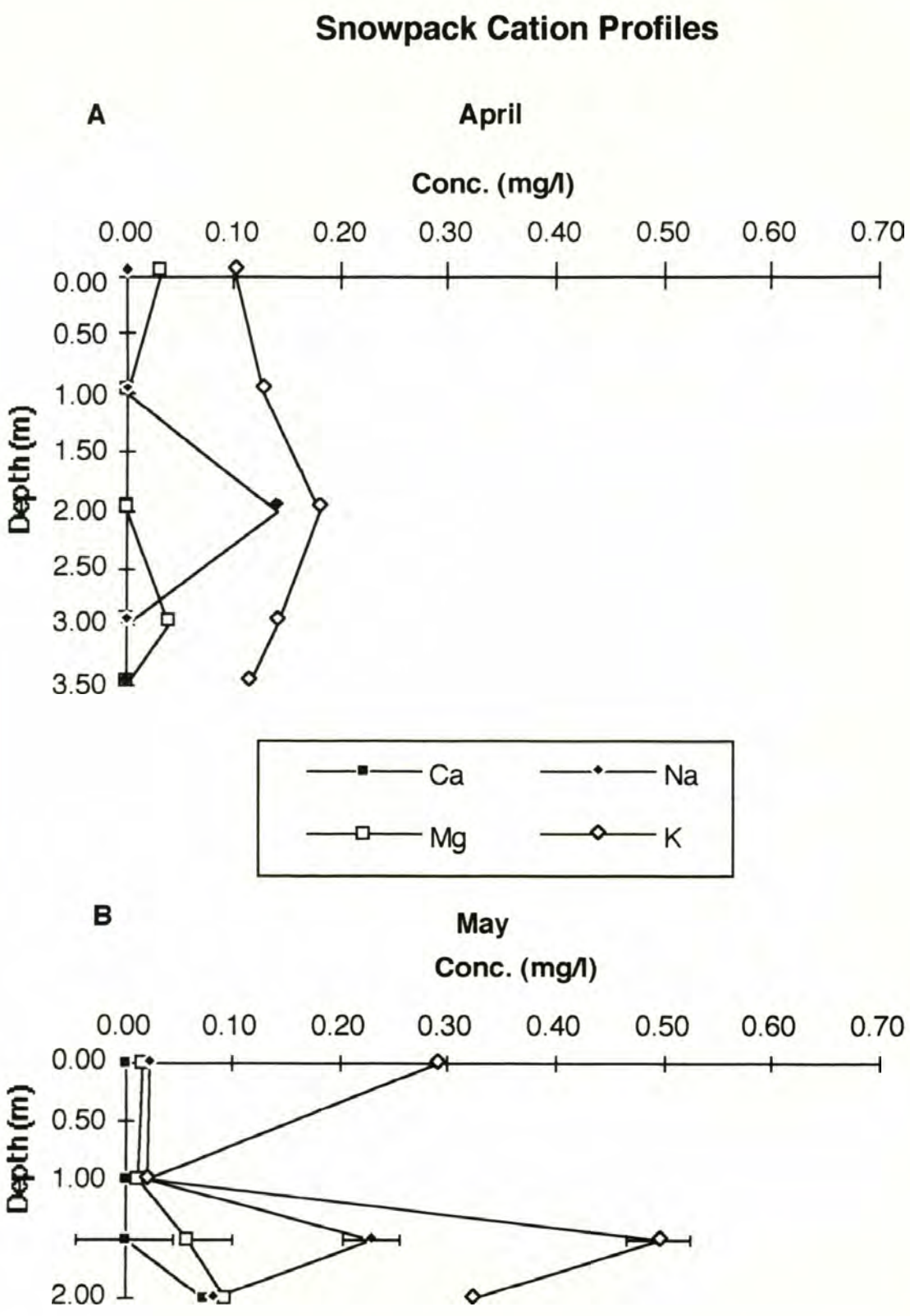


Figure 8: Snowpack profile showing cations for April (A) and May (B), 1992. Confidence intervals are shown for the data points from May at 1.5 m.

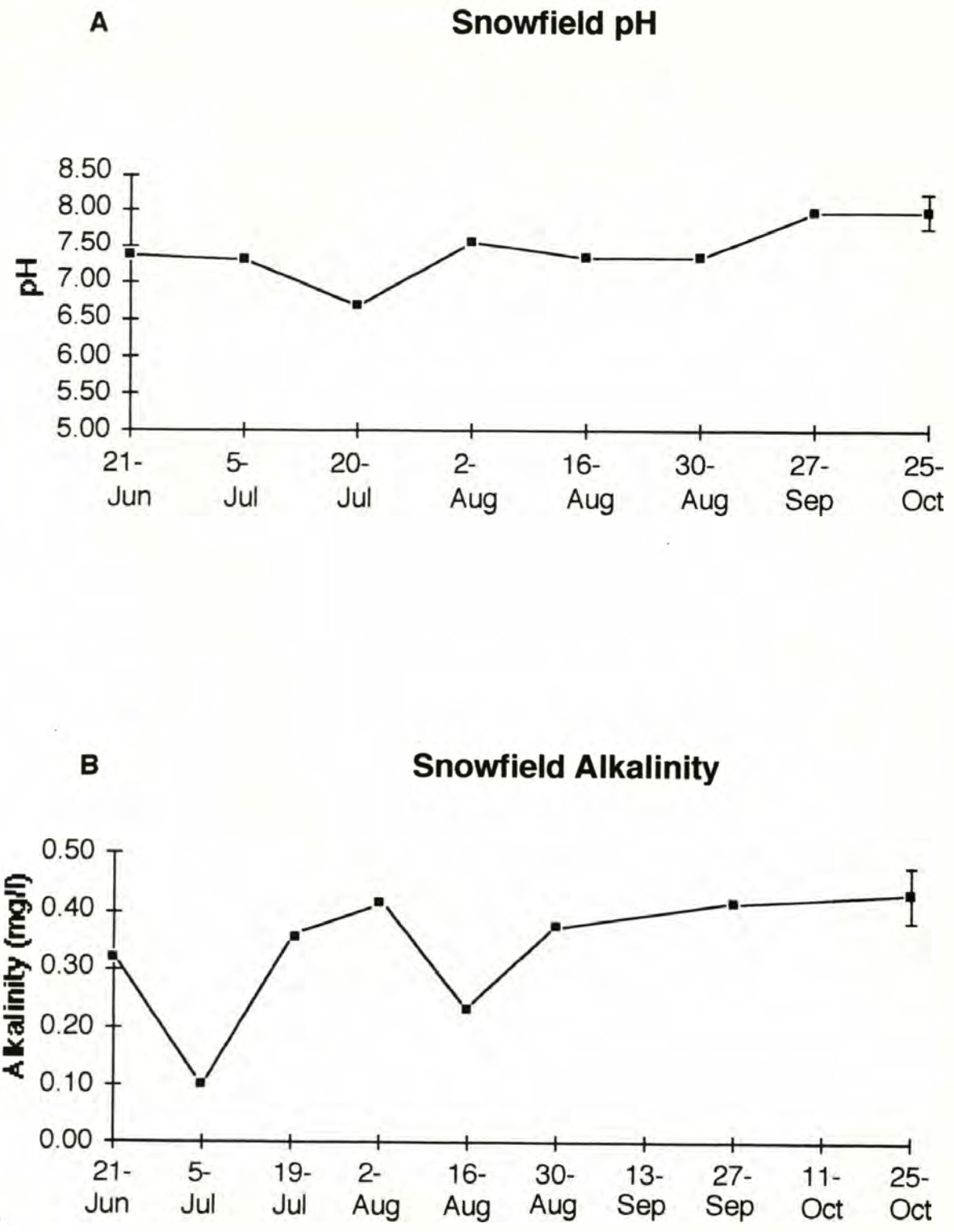


Figure 9: Variations for pH (A) and alkalinity (B) for a permanent snowfield in the Upper Bagley watershed.

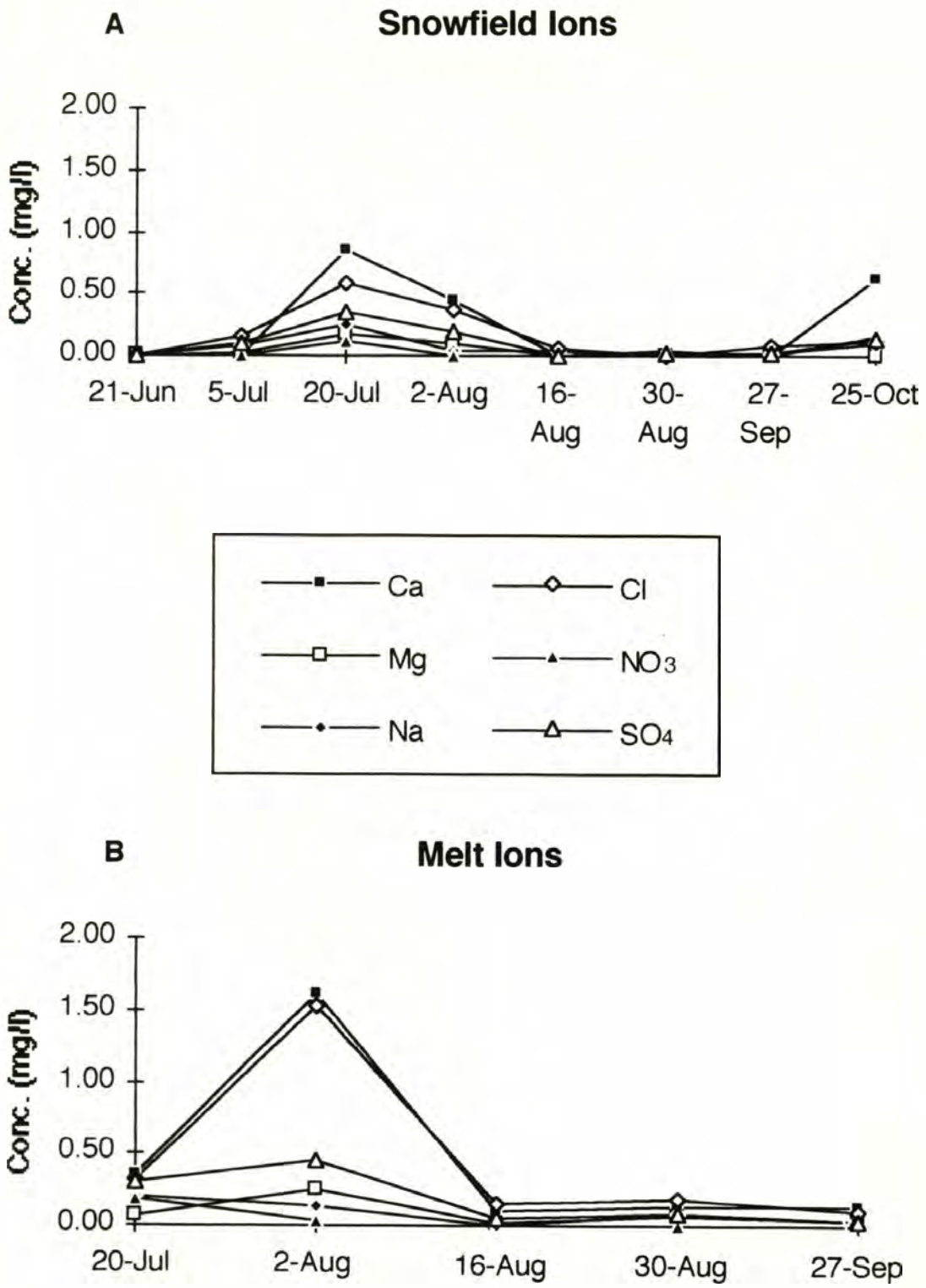


Figure 10: Major ion concentrations for snowfield ice (A) and melt-water collected from the snowfield (B).

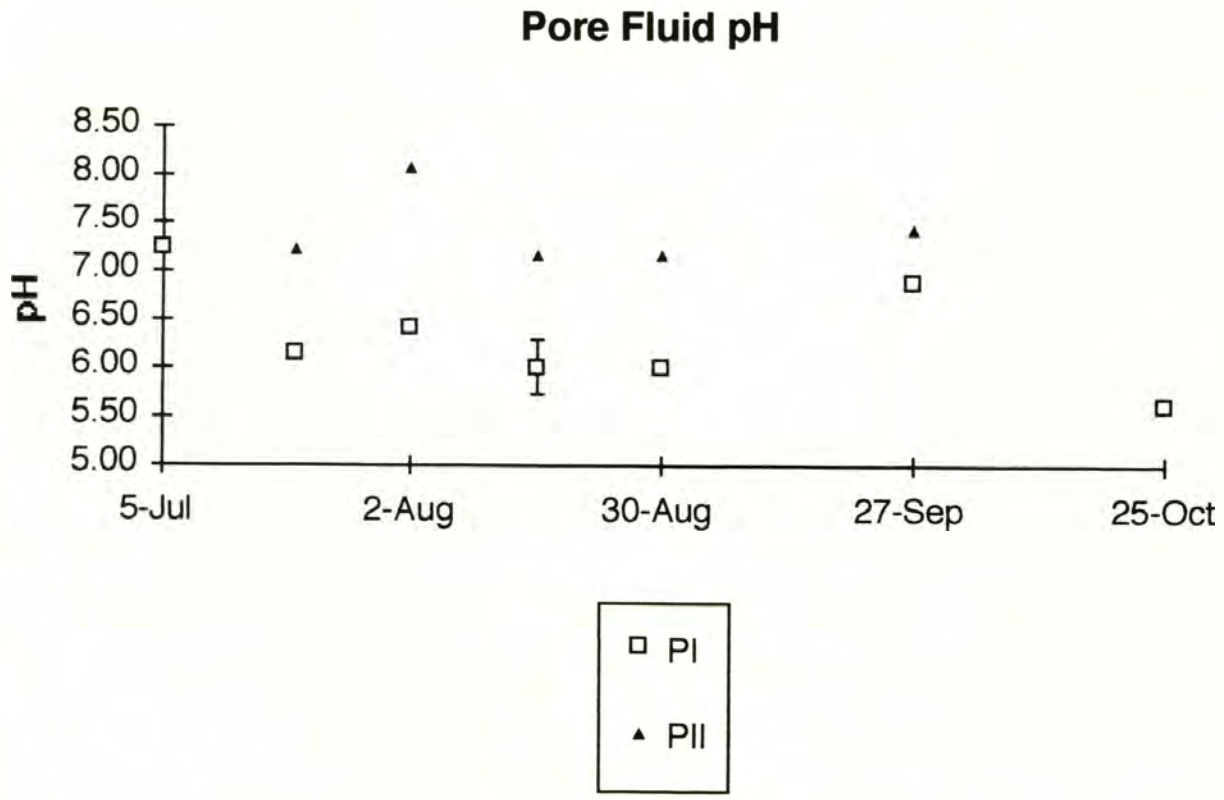


Figure 11: Variation of pH for Pore Fluid I and Pore Fluid II. The confidence interval for pH is shown for the August 16 Pore Fluid I sample.

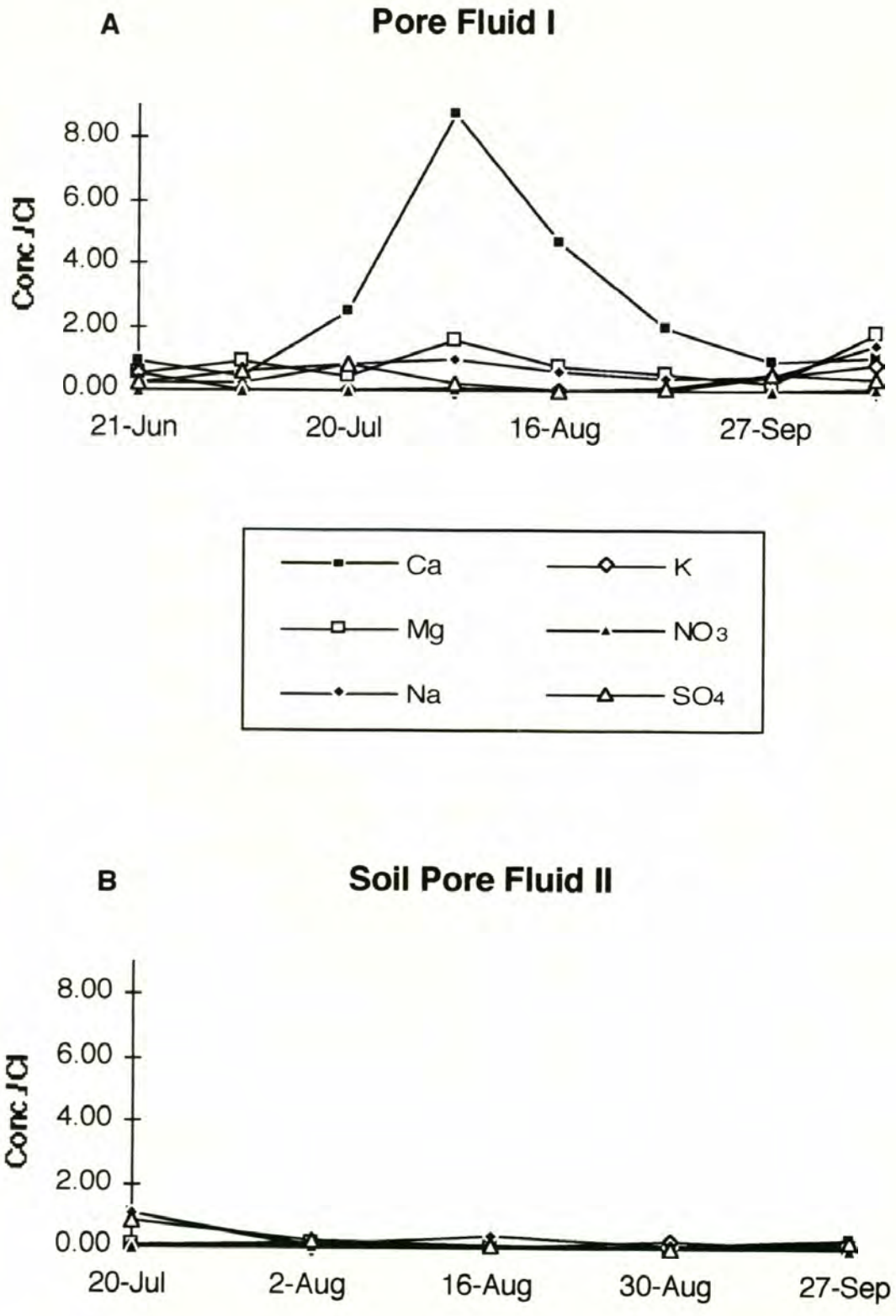


Figure 12: Major ion concentrations for pore fluids. Concentrations are corrected for dilution by dividing the ion concentrations by the chloride concentration for each sample. Data for Pore Fluid I are shown in A. Data for Pore Fluid II are shown in B.

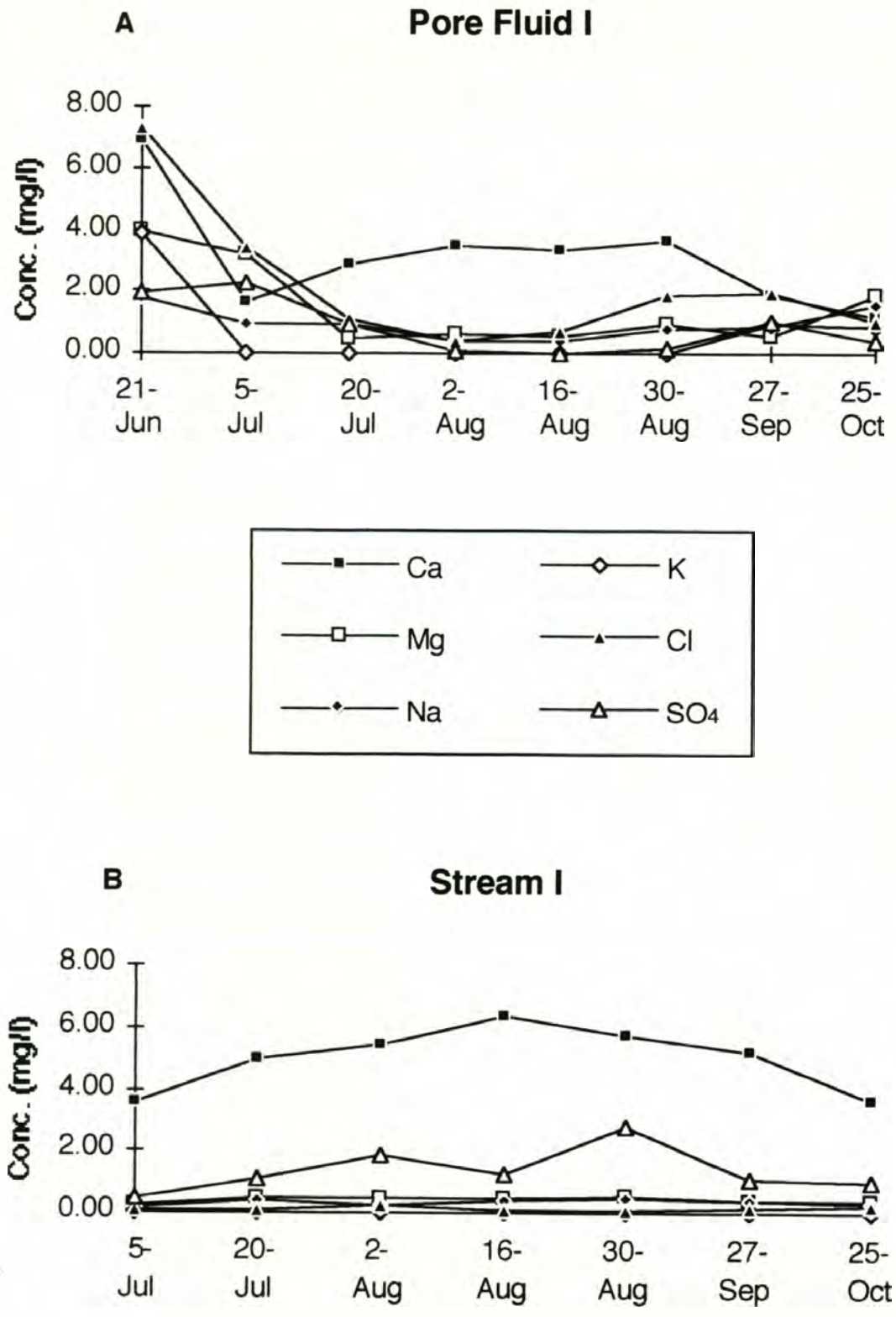


Figure 13: Major ion concentrations for Pore Fluid I (A) and an adjacent stream (B). Concentrations have not been corrected for dilution to show detail of potassium trends in Pore Fluid I.

Pore Fluid I was collected adjacent to a minor stream, referred to as Stream I. Stream I is a third order stream that has a low rate of discharge. The concentration of calcium in Stream I is as much as twice the concentration of calcium in Pore Fluid I (Figure 13). The concentration of calcium in Pore Fluid I increases mid-season, peaking in early August before declining. Calcium carbonate alkalinity becomes more dominant as calcium peaks in concentration (Figure 14A). The anions in Pore Fluid I are dominated by alkalinity. Stream I is dominated by sulfate (Figure 14B).

Pore Fluid II was collected down-slope from the snowfield that was sampled as part of this study, where melt-water had infiltrated the soil. The cations in Pore Fluid II are dominated by sodium (Figure 15A). There is no clear seasonal variation in this pore fluid, although sulfate increases in late fall (Figure 15B). The sulfate is derived in part from decaying vegetation.

Surface Runoff

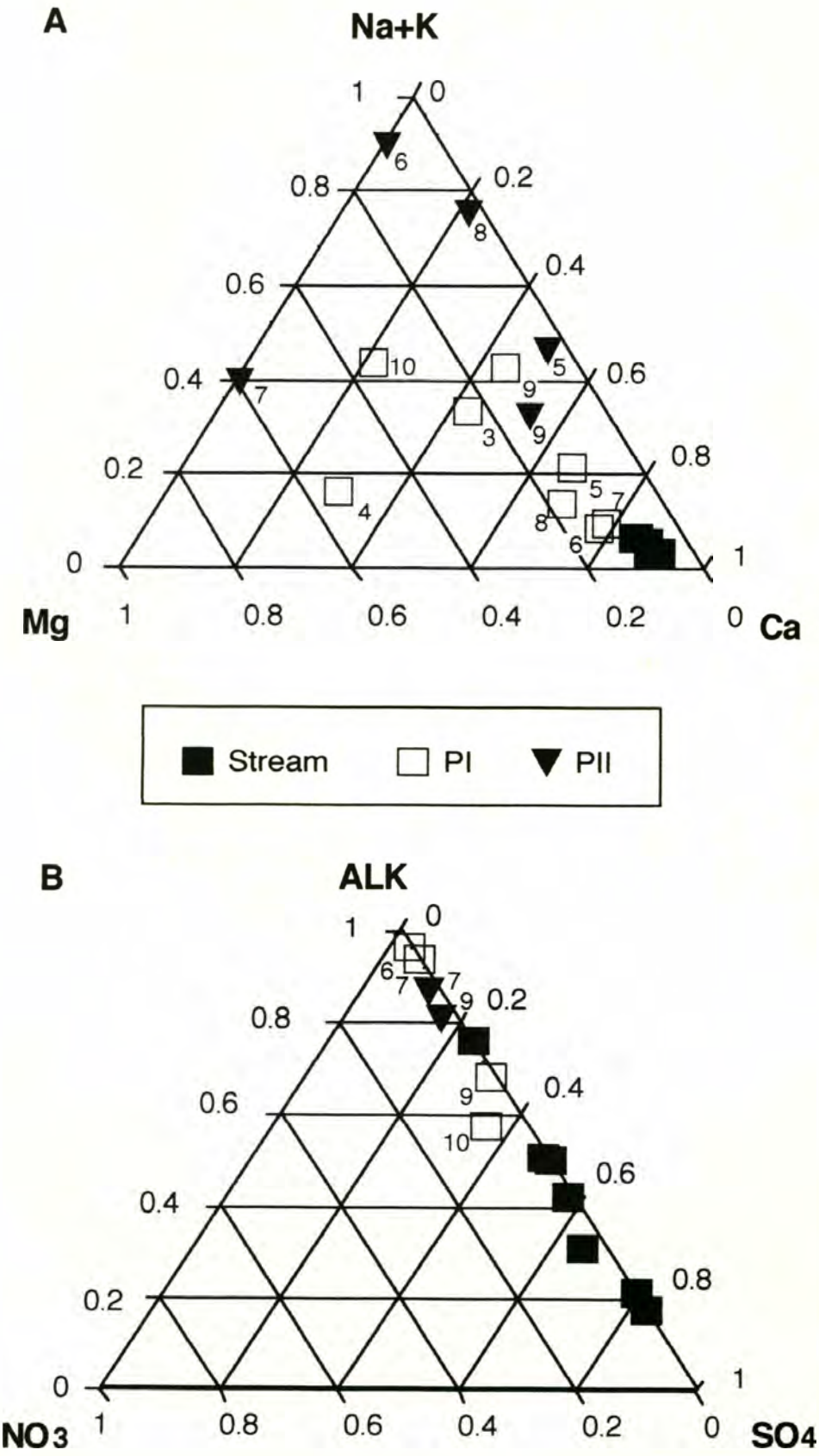
The inlet and outlet are chemically similar. Both plot in the same area on a ternary diagram, with calcium as the dominant cation (Figure 15A) and the anions dominated by alkalinity and sulfate (Figure 15B). When compared with ternary plots for snow (Figure 16) and pore fluids (Figure 14), outlet and inlet waters more closely resemble the chemistry of the pore fluids.

Figure 17 shows the fluctuations of ions over time for the inlet (A) and outlet (B). Ion concentrations have been corrected for chloride by dividing the concentration of each ion by the concentration of chloride in the same sample. Chloride is greater in pore fluids than in surface waters, resulting in scale differences between Figures 12 and 17 for the chloride-corrected ion

Figure 14: Ternary diagrams for pore fluid cations and anions. Data for Pore Fluid I, the stream adjacent to where Pore Fluid I was collected, and PII are shown. Ternary diagrams show relative concentrations of calcium, magnesium, and sodium combined with potassium (A), and of sulfate, nitrate, and alkalinity (B).

The small numbers adjacent to the symbols indicate the date the pore fluid samples were collected:

4	July 5
5	July 20
6	August 2
7	August 16
8	August 30
9	September 27
10	October 25


A
Na+K
Mg
Ca
Stream
PI
PII
B
ALK
NO3
SO4

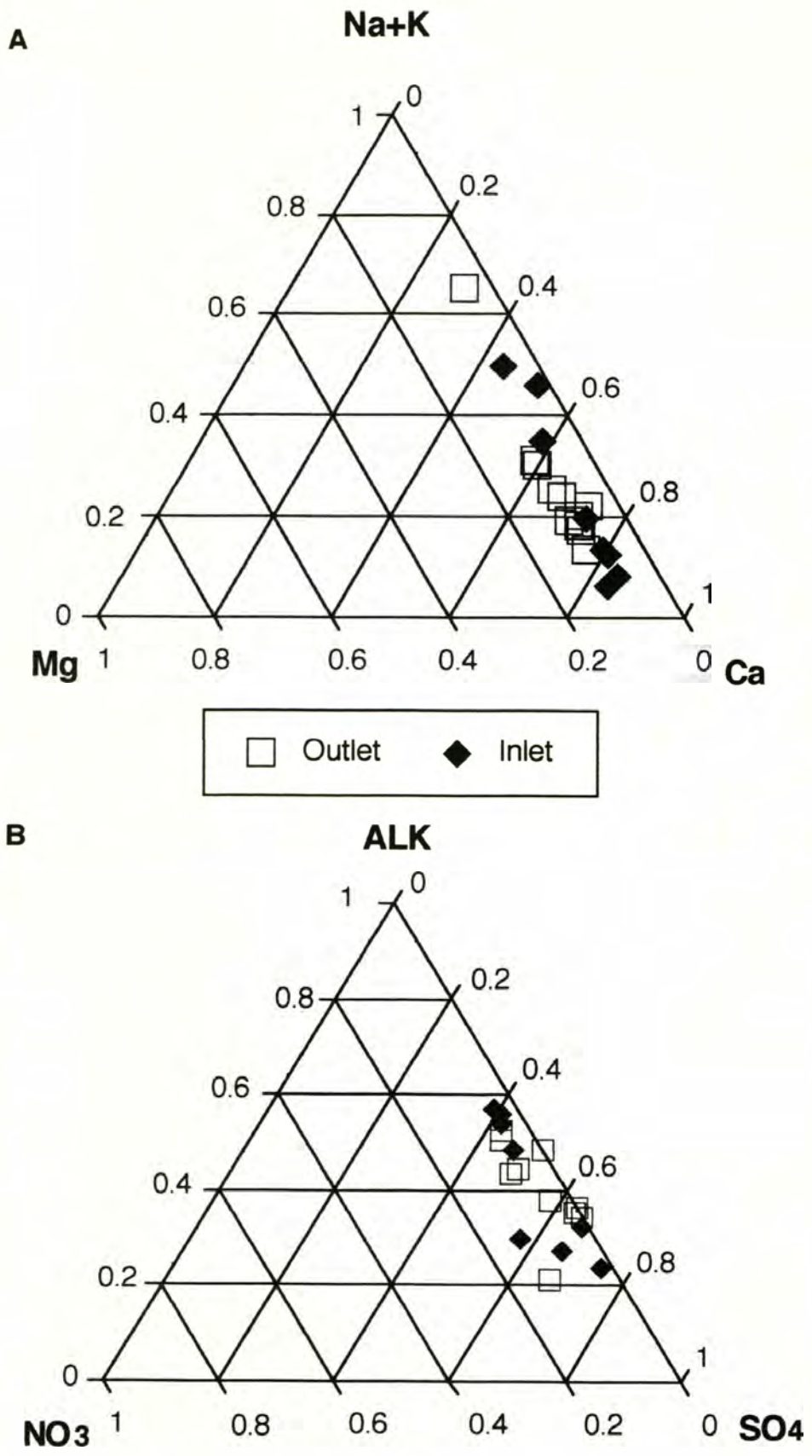
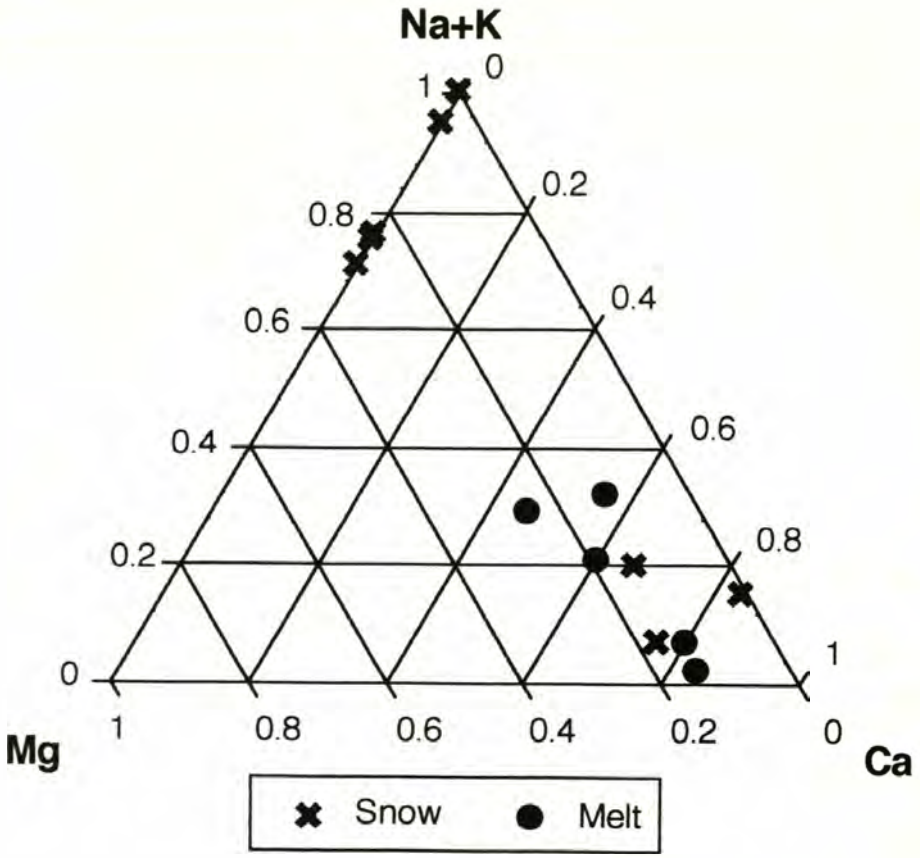


Figure 15 Ternary diagrams for outlet and inlet cations and anions.



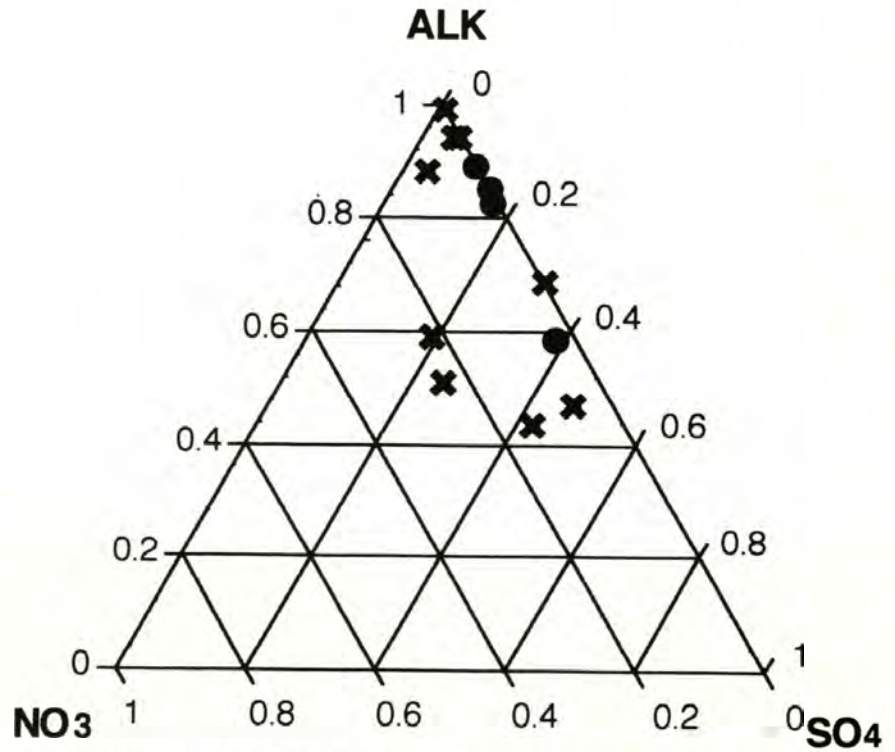


Figure 16: Ternary diagrams for snow and melt cations and anions.

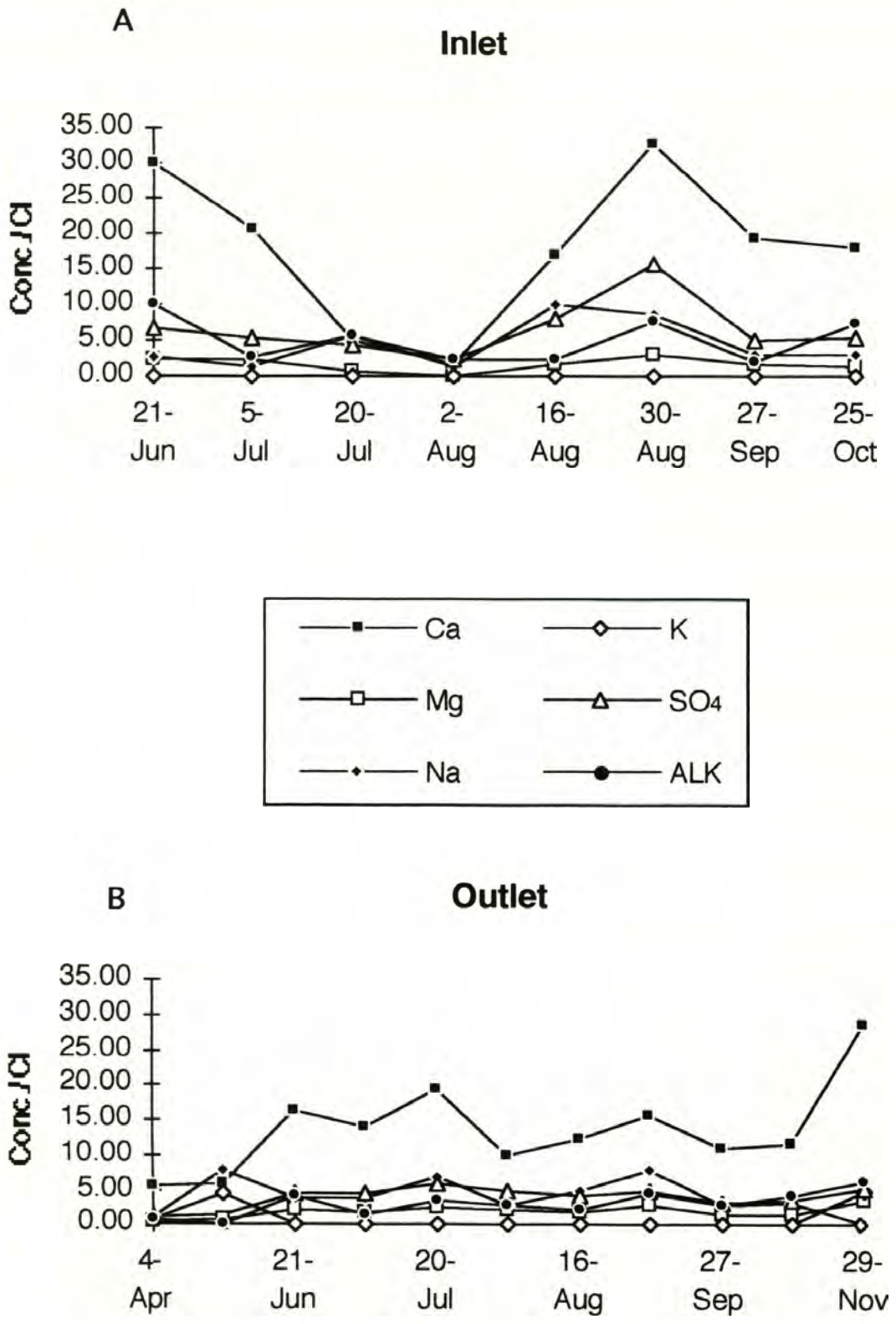


Figure 17: Major ion concentrations for inlet (A) and outlet (B). The concentrations have been corrected for chloride.

concentrations. The relatively high proportion of chloride in pore fluids is due to the greater residence time for water in soils. There is a decrease in calcium in late July and early August followed by a peak in late August.

Lake

Surface water samples were taken from the east and west ends and the middle of Upper Bagley Lake. The lake pH rises slightly during the growing season (Figure 18). Calcium is has the highest concentrations relative to the other ions (Figure 19A). Surface water samples from Upper Bagley Lake are chemically similar to the outlet samples. Chemical data for the lake (Figure 19) plot in the same area of a ternary diagram as those for the outlet (Figure 15).

Lake-sediment samples have a red-orange coloration from July to August. The coloration is caused by a film that can be seen in sediment samples kept in the laboratory. The film is associated with unidentified bacterium, as observed using transmitted light microscopy. As expected, ion concentrations are greater in the fluids extracted from the sediment than in the lake itself (Figure 20). Iron is present in measurable concentrations (Appendix 2), is associated with the orange film in the sediments.

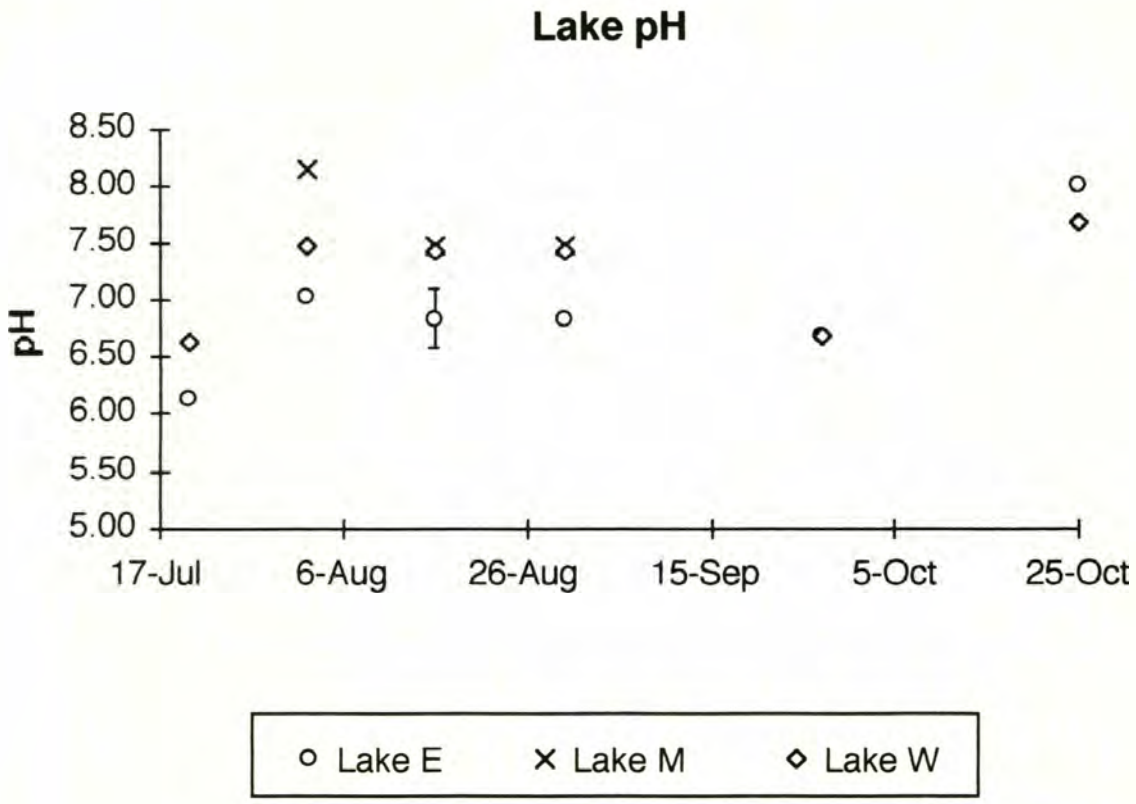


Figure 18: Lake pH over time for east, middle, and west sites. The confidence interval for pH is shown for the August 16 data point from the east site.

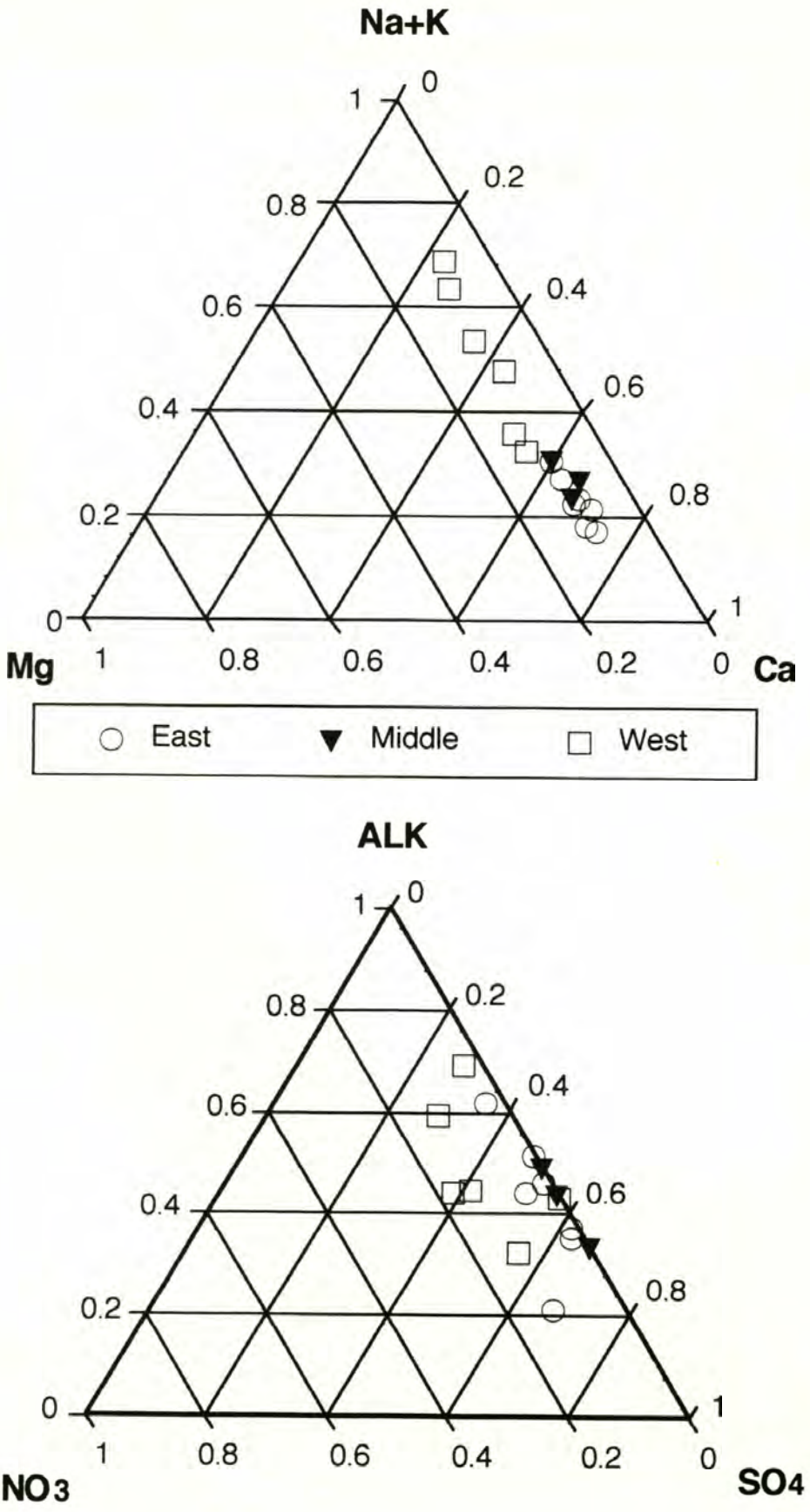


Figure 19: Ternary diagrams for east, west and mid-lake cations and anions.

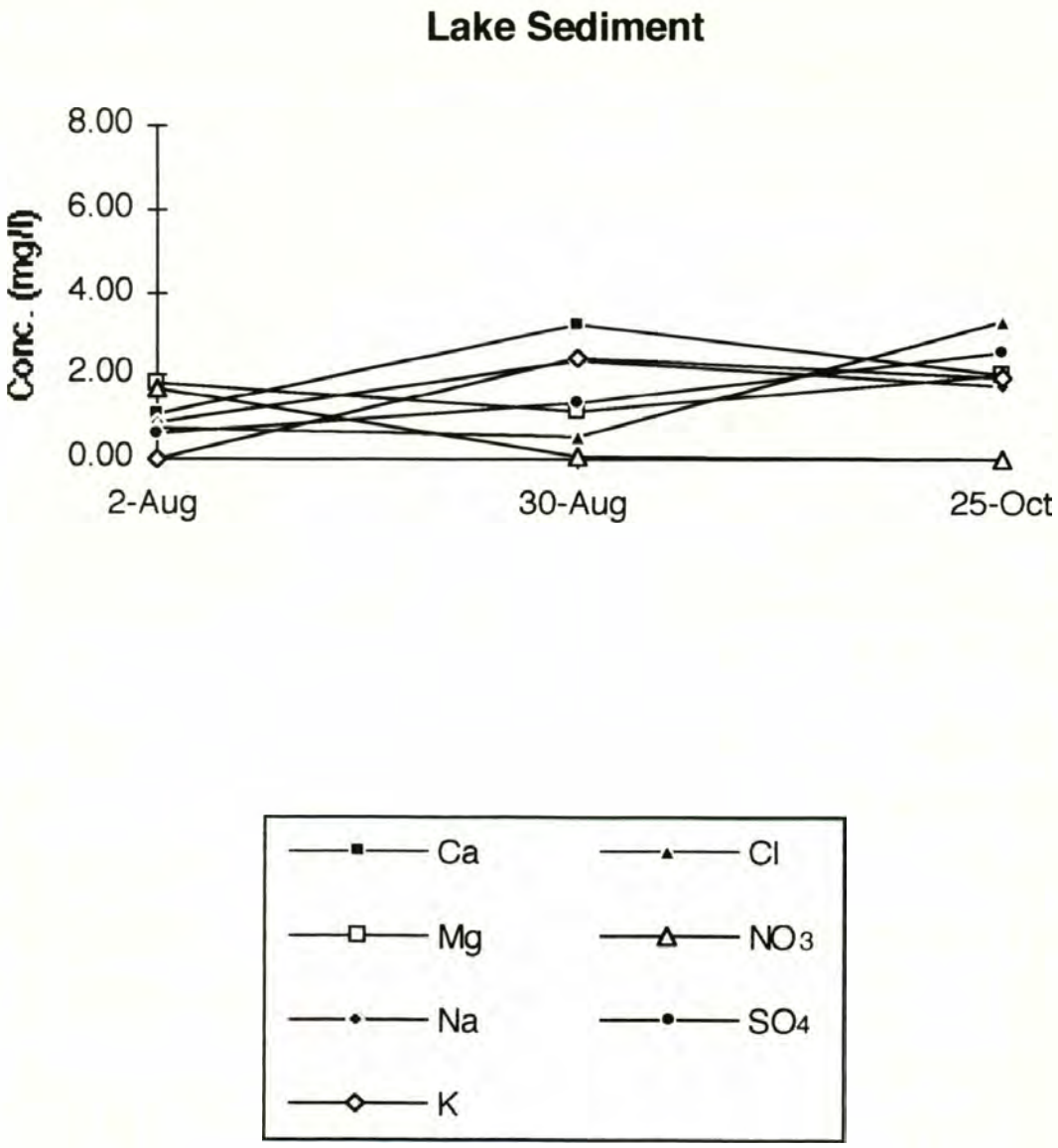


Figure 20: Major ion concentrations for fluid extracted from lake sediments.

Soils

A summary of soil characteristics for Soil types I and II is given in Table 3. The only clay mineral detected by x-ray diffraction in Soil I is montmorillonite, a "swelling" clay that can take up water between its structural layers. Montmorillonite forms from alteration of igneous rocks, usually tuffs or volcanic ash. The cation exchange capacity ranges from 80 to 150 meq/l (Deer et al., 1966).

Table 3: Soil Characteristics

	Soil I	Soil II
Classification*	Aquent	Psamment
Texture	Clay loam	Gravely sandy loam
Consistency	Sticky, nonplastic	Loose
Color (moist)	Dusky yellowish brown (10 YR 2/2); Moderate reddish brown (10 R 4/6) mottling	Olive black (5 Y 2/1)
Composition	Montmorillonite Inorganic colloids Organic acids	Andesine Inorganic colloids Minor Quartz
Origin	Glacial till and volcanic ash	Andesite talus
pH	5.55	5.52
Depth	< 1 m	< 1 m
Vegetation	Heather, sedge, huckleberry	--
Root Depth	10 cm	--

*Soil Survey Staff (1975)

The clay and silt fractions of the Soil I are dominated by amorphous inorganic colloids and organic acids with a minor amount of plagioclase in the

silt fraction. Soil I periodically has reddish-orange mottling during the growing season. Measurable iron is present in Pore Fluid I when mottling is present.

The mineralogy of Soil II reflects its andesite source. The clay and silt fractions of this soil are composed primarily of inorganic colloids and andesine, a plagioclase feldspar. The silt fraction includes some quartz, probably derived from the Chilliwack Greenstone elsewhere in the basin. X-ray diffraction reveals no clay minerals in Soil II.

Soil Leachates

The results of the soil leachate experiments are given in Appendix 3. Potassium was absent from fluids extracted from both columns. Concentrations for the other ions increase in both columns (Figure 21). Concentrations of calcium, nitrate, and sulfate are greater in fluids from Soil I. Calcium and sulfate concentrations are as much as five times greater in the solution from Soil I than that from Soil II. No measurable iron is present in either soil solution.

Plant Leachates

Data from the plant leachate experiment are given in Appendix 4. Grass has a greater total ion concentration than heather and has a more evenly distributed range of ions (Figure 22). Potassium accounts for 78 percent of the ions leached from heather and 21 percent of the ions leached from grass. Heather contributes more potassium per gram of plant material than grass.

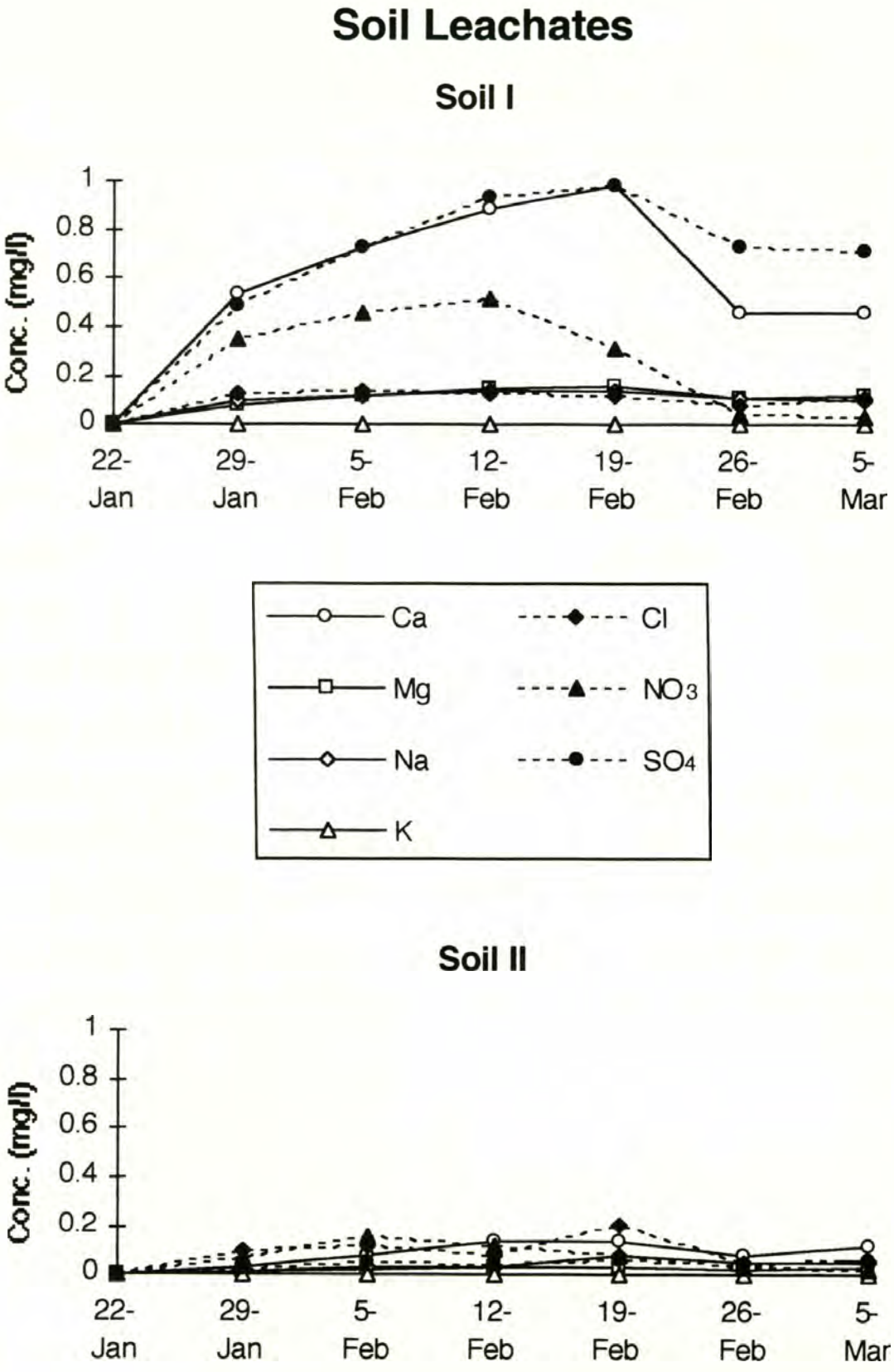


Figure 21: Major ion concentrations for soil leachates.

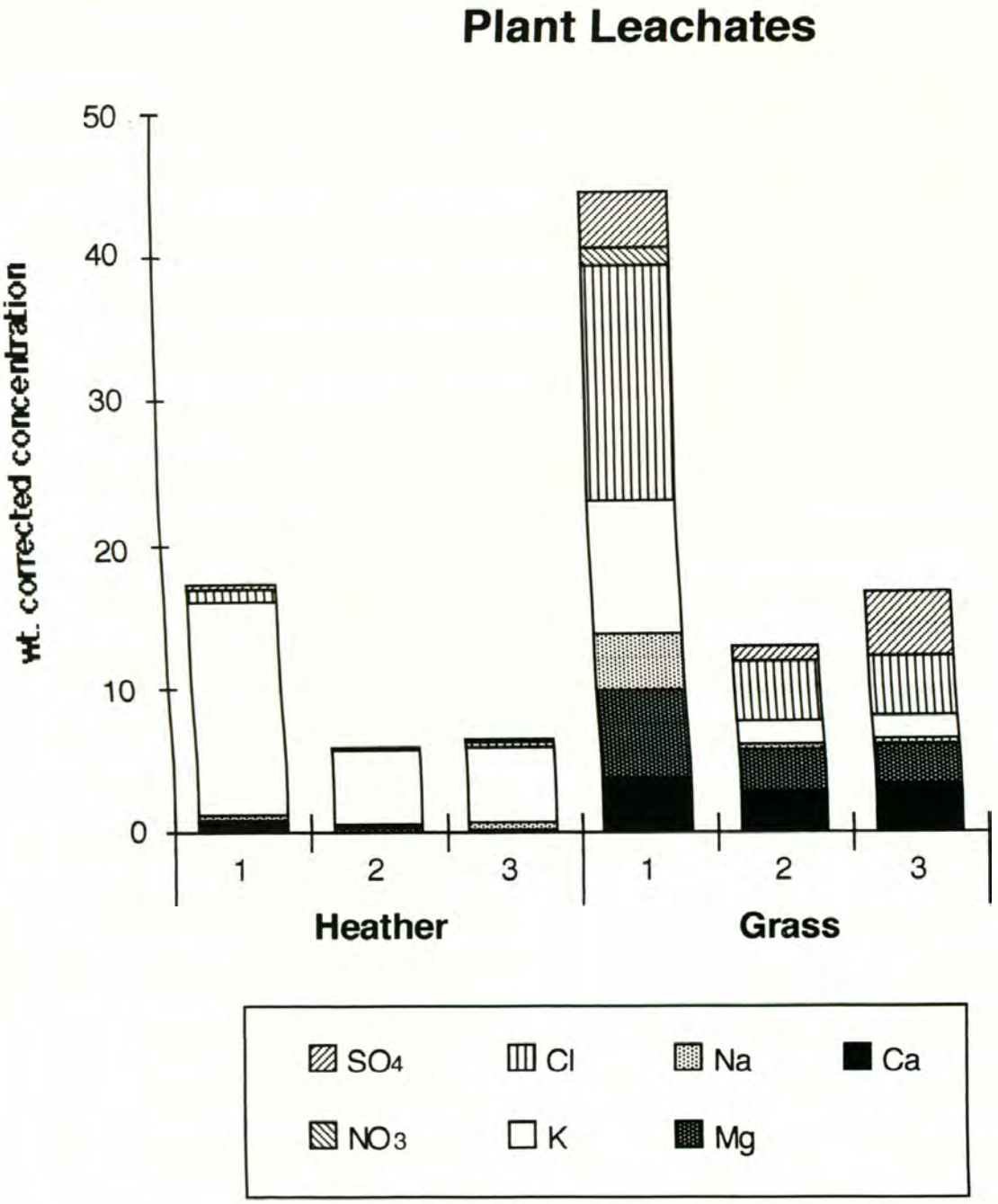


Figure 22: Plant leachates for heather and grass. Replicates for each plant are labeled 1 through 3. The weight corrected concentrations were calculated as:

$$\frac{\text{ion concentration}}{\text{volume of water} \cdot \text{mass of plant material}}$$

IV. DISCUSSION

Ion Sources

According to Dethier (1979), precipitation loading accounts for 30 percent of the major ions found for typical North Cascade streams originating from subalpine catchments. Major ions include hydrogen, calcium, magnesium, sodium, potassium, chloride, nitrate, and sulfate. Calcium and potassium are derived largely from continentally derived aerosols. Sodium, magnesium, chloride, and sulfate are derived from marine aerosols. Nitrate originates from plant and bacterial fixation of nitrogen from the atmosphere and input from precipitation. Sulfate, nitrate, and hydrogen are in part derived from anthropogenic pollutants. An additional source for sulfate and hydrogen in the Upper Bagley watershed is steam from Mount Baker, an active volcano located approximately 10 km southwest of the lake.

Atmospheric contributions to the ion pool in a watershed are often acid salts such as H_2SO_4, HNO_3, and HCl. These acids react with soil and rock surfaces in the watershed, stripping off cations, a process called cationic denudation (Likens et al., 1977). Cations originating from rock and soil in the Upper Bagley basin include calcium and sodium from andesine. The cations form neutral salts, $CaSO_4$, Na_2SO_4, and $Mg(NO_3)_2$, with the anions contributed by the atmosphere.

Ions are stored in an alpine watershed as snowpack from late fall to early spring. There are three paths the melt can take in reaching the lake: 1) the melt infiltrates the soil and flows through as a pore fluid, 2) during storm events, the melt combines with precipitation as Horton Overland Flow or saturated surface flow, or 3) the melt enters a stream and flows to the lake as channelized flow.

After infiltration, soil solutions become enriched in major ions through interaction with the surfaces of soil particles. Ions are stored in the watershed as pore fluids and, during storm events or periods of peak snowmelt, enter stream channels, significantly altering the chemistry of the stream. Stream water can be considered a mixture of pore fluids. The proportion of pore fluids that contributes to surface water chemistry depends upon the prevailing hydrological conditions (Christophersen & Neal, 1990). The chemistry of Horton Overland Flow is uninfluenced by pore fluids relative to direct precipitation because the interaction between soil and water is reduced in this short-term, high volume flow. The chemical contribution of Horton Overland Flow to Upper Bagley Lake is not discussed in this study.

As discussed in the section on soil-water interaction, soil and vegetation serve as both a source and a sink of ions in the Upper Bagley watershed. Calcium, sulfate, and nitrate increase markedly in water in contact with Soil I (Figure 21). The plant leachate experiment (Figure 22) demonstrates that vegetation can make a significant contribution to the chemistry of surface waters. The effects of leaching are more pronounced in Stream I (Figure 13) relative to other streams as it is stagnant between storms. Increased residence time for water in Stream I allows more time for the underlying soil and the adjacent heather and grasses to be leached.

Once in the lake, ions are stored in the water column or are trapped in lake-bottom sediment. Water in direct contact with the lake sediments becomes enriched in most major ions (Figure 20) as well as iron (Appendix 2), suggesting that the sediments act a source as well as a sink of ions. Calcium, magnesium, sodium, chloride, and sulfate are also concentrated in water bodies through evaporation.

Groundwater can have a significant impact on the chemistry of a lake as a contributor as well as a sink for ions. Groundwater chemistry, however, is not within the scope of this study.

Snow - Melt Dynamics

Other studies show that the melt fraction of snow is enriched in ions relative to the ice fraction. Sodium, potassium, calcium, magnesium, nitrate, sulfate, and chloride are three to five times more concentrated in melt-water than in snow at various sites in Norway (Johannessen & Henriksen, 1978). During and after snowmelt, the sulfate concentration in Filson Creek, Minnesota, increases from 2 to 14 mg/l and pH decreases from 6.6 to 5.5 (Siegel, 1981). Ions are two to ten times more concentrated in melt water than in snow in the Turkey Lakes watershed in Ontario (Semkin & Jeffries, 1986). The high ion concentrations in the melt fraction of the snowpack are attributed to a "freeze-concentration" process during snow recrystallization and melting in which contaminants accumulate preferentially at the surface of ice crystals in the snowpack (Johannessen & Henriksen, 1978). The melt-water then interacts with the the ice crystals, producing a "surface effect" in which the melt acquires excess ions from the surface of the ice.

In the Upper Bagley watershed, the chemical profile of the snowpack and the chemical changes that occur in the snowfield result from the surface effect between ice and melt. The inflection of pH at depths of 1.5 and 2 m in the snowpack in April and May, respectively (Figure 6), are caused by the interaction between melting snow and ice crystals. The depth at which calcium, sodium, sulfate, and nitrate become more concentrated and pH decreases is interpreted to be the maximum depth of penetration for melt percolating downward through the snowpack.

In April, alkalinity decreases at a depth that corresponds to the negative pH inflection. An direct relationship between pH and alkalinity is predicted using the definition for carbonate alkalinity (Stumm & Morgan, 1981):

$$[ALK] = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+] \quad (4)$$

Hydrogen ions increase as pH decreases. When hydrogen ions increase, alkalinity decreases because $[H^+]$ is negative on the right hand side of Equation 2. The pH and alkalinity data for the snowfield also show a positive relationship as expected.

It is assumed that the inflection point for pH and alkalinity occurs at the maximum depth of penetration for melt-water from the surface of the snow. Melt forming at the base of the snowpack because of thermal diffusion from the ground would tend to flow along the base of the snow without impacting the rest of the snowpack.

Nitrate in the snowpack declines slightly at depth from the surface concentration. Nitrate is lost through the migration of meltwater through the snowpack or through denitrification by microbial processes, transforming nitrate to nitrite:

$$C_6H_{12}O_6 + 12\,NO_3^- \rightarrow 12\,NO_2^- + 6\,CO_2 + 6\,H_2O \quad (5)$$

If nitrate is lost only through snowmelt, a peak concentration for nitrate would correspond with the inflection depth for the other anions. The steady decline of nitrate suggests that nitrate is lost through microbial action.

For denitrification to occur, there needs to be a source of organic carbon ($C_6H_{12}O_6$) and the environment needs to be anaerobic. Continentally derived aerosols trapped in the snowpack are a probable source for organic carbon. Denitrifying bacteria metabolize in environments that are anoxic or have very low oxygen. It is assumed that the snowpack has been sufficiently compacted at depths of greater than 1m to remove most air pockets that include oxygen.

The limited oxygen available in the compacted snowpack can be depleted by other bacteria present in the snow. A more thorough test of this hypothesis would be to observe how sulfide concentrations vary because sulfate is converted to sulfide under anaerobic conditions. If sulfide increases relative to sulfate, then the snowpack is depleted in oxygen.

Melt water from the snowfield has greater concentrations of major ions than the ice, suggesting that ice-water interaction is still significant in snow that is not fresh. Distribution coefficients (Kd) for the snowfield are calculated as:

$$K_d = [Melt] / [Ice] \quad (6)$$

where [Melt] is the concentration of a given ion in melt water and [Ice] is the concentration of the same ion in the snow. Distribution coefficients are given in Table 4.

Table 4: Distribution coefficients for snow and melt water

	Ca	Mg	Na	K	Cl	NO_3	SO_4	ALK
20-Jul	0.42	0.42	0.76	0.00	0.54	1.64	0.86	-
2-Aug	3.66	2.72	3.67	0.00	4.11	m	2.36	1.67
16-Aug	m	m	1.18	0.00	1.46	0.00	3.09	1.13
30-Aug	m	m	1.00	0.00	m	i	2.96	1.00
27-Sep	m	6.33	3.05	0.00	2.19	0.87	4.32	1.02

K_d is 0 if the ion in the melt fraction or the ice fraction has a concentration of 0 mg/l. In Table 4, K_d is designated as m where the ion concentration of the melt fraction is greater than 0 and the ion concentration of the ice is 0. The Kd is designated as i where the ion concentration of the ice fraction is greater than 0. The K_d for potassium is 0 in all samples, since this ion is not present in measurable concentrations in ice or melt samples.

In the July sample, K_d is less than one for calcium, magnesium, sodium, chloride, and sulfate, indicating that the ice is enriched in these ions relative to the melt fraction. Subsequent sampling dates have K_d values greater than one for the same ions. A K_d value greater than one indicates enrichment of the melt relative to snow. In September, the melt-water is enriched by a factor of 6 in magnesium and by a factor of 4 in sulfate relative to snow. In early August, the melt-water is enriched by a factor of 3 in calcium and sodium and by a factor of 4 in chloride. The values for calcium, magnesium, sodium, chloride, and sulfate are subject to temperature and precipitation. Rapid melting due to elevated temperatures reduces the surface effect between water and ice as the volume of water increases. The decreased surface effect decreases the K_d. The low distribution coefficients of July 20 can be attributed to the elevated daily average temperature at that time. Subsequent sample dates had lower daily average temperatures.

Alkalinity and nitrate do not respond to water-ice interaction in the same manner as other ions. The Kd for values for alkalinity and nitrate are close to one, suggesting that water-ice interaction does not affect the concentration of either. The interaction of water and ice does not affect alkalinity or nitrate because the concentrations are primarily controlled by external parameters. The equilibria of the other major ions are internally controlled in the system that consists of ice and meltwater. The equilibrium of alkalinity is primarily controlled by the interaction of the ice surface with CO_2 in the atmosphere. Nitrate is controlled by bacterial transformations as previously discussed.

Soil-Water Interaction

Chemical tracer studies (Ahuja et al., 1981; Stewart & McDonnel, 1991) indicate that pore fluids may have long residential times and contribute significantly to storm-flow. Mixing with rainwater occurs predominantly in the upper 50 mm of the soil, but the depth of mixing fluctuates with changes in discharge. The transfer of ions from below the thin mixing layer is due in part to the turbulence produced by raindrop impact, resulting in an accelerated diffusion process (Ahuja & Lehman, 1983). Pore fluids are significant ion reservoirs in watersheds and overprint the chemistry of precipitation with ions leached from the soil during prolonged residence times.

Soil I and Soil II have different compositions and undergo different reactions in the presence of water. Soil I is comprised of sodium montmorillonite, inorganic colloids, and organic acids. Soil II is dominated by andesine and inorganic colloids as it is a more primitive soil.

Montmorillonite is a swelling clay, taking up water molecules between its structural layers and expanding. The water storage capacity of Soil I is augmented by the presence of this clay mineral, increasing the time that solutions are in contact with the soil, increasing the concentration of leachable ions that solutions remove from the soil. The most common exchangeable cations in montmorillonite are sodium and calcium, although potassium and magnesium are also involved in cation exchange with this clay (Deer et al., 1966). Montmorillonite will preferentially take up the divalent calcium cations between its structural layers Exchangeable cations are released into solution as pH decreases because hydrogen ions displace other cations.

The colloids and organic acids in Soil I provide exchangeable sulfate, nitrate, and iron to soil solutions. Oxidation of samples during handling may change the chemistry of the pore fluids, especially impacting sulfate, pH, and

alkalinity (Arthur, 1992). The soil is a reducing environment in which S^0, NH_4^+, and Fe^{3+} compounds are stable. When in contact with water, the soil becomes an oxidizing environment, resulting in the transformation of S^0 to $SO_4^=$, NH_4^+ to NO_3^- and Fe^{2+} to Fe^{3+}. In the laboratory soil leachate experiment, the increase in calcium appears to follow the same pattern as the increase in sulfate (Figure 21). Field data indicate that as pH decreases (Figure 11), the leaching of calcium from vegetation and Soil I increases (Figure 12). The increase in leached calcium ions in the field measurements is not accompanied by an increase in leached sulfate ions. The soil in this instance is a reducing environment in which the most stable sulfur ion is sulfide.

Plant material contributes some major ions to the soil. Sulfate, calcium, magnesium, and nitrogen have been shown to be contributed by vegetation (Abrahamsen, 1980; Tian et al., 1992). The potassium in Pore Fluid I during snowmelt and late in the growing season is contributed by decaying vegetation. As demonstrated by the plant-leaching experiments (Figure 22), heather contributes a larger proportion of this ion per weight than does grass but plays a minor role in contributing other ions to solution. Potassium that is released into soil solutions is taken up and stored in vegetation through the growing season. Other ions that are contributed by grass include chloride, magnesium, sulfate, and calcium. The ions leached from decaying vegetation can be stored in pore fluids in the soil to be released when precipitation from a moderate- to high-intensity storm flushes the soil or can be taken up by subsequent plant growth and stored in plant tissues.

Subsystem Interaction

The Upper Bagley watershed has been described in this study as a series of geochemical subsystems, each with its own series of chemical

reactions that transform ions that enter it. These subsystems are not isolated but rather interact with each other. An example of subsystem interaction is the exchange between soil solutions and surface water. Wallach and van Genuchten (1990) developed a model that predicts concentrations for chemicals released into overland runoff by rainfall. The model takes into account convective-dispersive solute transport in the soil and a rate-limited mass transfer through a laminar boundary. The laminar boundary layer is at the soil surface-runoff water interface.

Robson et al. (1993) provide another example of the interaction between soil solutions and surface water. Storm events with high conductivity precipitation were used to trace the path of rainwater entering streams. For events producing low flow (less than 1mm/hr), the chemistry of the rainwater was not observed in the stream. In high-flow events the chemistry of the rainfall influenced the stream and impacts the storm-flow chemistry of subsequent storms. A strong differentiation of water types is indicated by the chemical data. Comparison of acidity to conductivity suggests that the acidity of the rain water is removed by catchment soils.

The increased concentrations of calcium in the watershed may be due in part to the mixing of one component of the watershed with another. For instance, the peak in the inlet calcium in late August may correspond with the peak in pore fluid calcium seen in early August. The time delay between the pore fluid and inlet calcium peaks implies that the residence time of water in Soil I is twenty to thirty days. There is a increase in outlet calcium in late November. The timing of this increase is probably not due to residence time of water in Upper Bagley Lake. The lake is shallow and flushes rapidly (Loranger, 1986). The watershed did not receive significant snow until late October; therefore, a restricted volume of inflow to the lake due to snow cover can not

explain a calcium residence time of three months. The slight increase in calcium in the outlet is probably not significant.

Mulder et al. (1990) utilized chemically inert chloride to model storage and mixing of pore fluids in soils in the Birkenes watershed in Norway. A layer of chloride was deposited on wet soil during a high-salinity rainstorm. The ensuing pulse of chloride was traced for a week in the upper soil layers before a rainfall of 24 mm diluted the pulse through flow from the soil to the stream and through vertical percolation. Soil-solution pathways were further studied at Birkenes using point-source injections of chloride (Müller et al.,1993). Müller et al. (1993) found that stream chemistry at Birkenes can be explained in part by the dynamic transportation of soil solutions. The residence time during the tracer experiments was assumed to be insufficient to see the effects of classic equilibrium exchange between ions.

Chloride was assumed to be a relatively inert ion in Birkenes, a chemically dilute watershed. No laboratory or field tests independent of the tracer studies were cited by Mulder et al. (1990) or by Müller et al. (1993) to confirm that chloride is a conservative ion. Like Birkenes, the Upper Bagley watershed is an ultrapure system. There is no indication based on field data from the Upper Bagley watershed that there is a source or sink for chloride in the biota. There are no unusual fluctuations of chloride relative to other ions. Fluctuations in chloride appear to be influenced by discharge only. The assumption that chloride is a conservative ion is therefore valid for the Upper Bagley watershed

Mixing

Christopherson and Neal (1990) developed End-Member Mixing Analysis (EMMA) to explain surface-water chemistry in terms of a mixture of soil

solutions at Birkenes. The model used in their study includes two distinct soil environments, shallow soils and deeper soil layers, that contribute to runoff chemistry. The main conclusion of Christophersen and Neal (1990) is that storm-flow water is derived in a large part from pre-event water stored as pore fluids that strongly modify the subsequent precipitation chemistry.

The EMMA approach utilizes mixing diagrams, with ion concentrations plotted against a conservative ion such as hydrogen, to show surface water as a product between different end-members. A modified EMMA approach, using log-log plots instead of normal grid plots, is applied here to the Upper Bagley watershed. Chloride is used as the conservative ion. Mixing end-members recognized include 1) snow and melt, 2) Pore Fluid I, 3) Pore Fluid II, and 4) Stream I. The mixing end-members plot in clusters. Snow and melt are low in chloride and cation concentrations. Pore Fluid I is high in chloride and cation concentrations. Pore Fluid II has high chloride concentrations and low in cation concentrations. Stream I has low chloride concentrations and high in cation concentrations. Lake sediments are another probable end-member; however, there were only three data points, to few for any substantial conclusions. High chloride concentrations for the pore fluids indicate a greater residence time for soil solutions than for other solutions in the watershed.

The mixing diagrams are correlation diagrams and are more effective if there is a strong correlation between the variables used in the plot. Correlation coefficients were calculated for chloride and ion concentrations for field sample analyses using Pearson's r. The $r_{crit\ [0.05,90]}$ is 0.205 (Helsel & Hirsch, 1992). A correlation coefficient that is greater than 0.205 indicates that there is a significant correlation between the two variables being used. A significant correlation determined using Pearson's r does not show cause, only a relationship. For example, the correlation coefficient for chloride and calcium is

0.225; however, an increase in the concentration of chloride does not necessarily cause a decrease in the concentration of calcium.

As indicated by their correlation coefficient, there is a significant correlation between chloride and calcium (Figure 23). Solutions from snow and melt are depleted in calcium and chloride. Pore Fluid II is enriched in calcium and chloride relative to snow but has low calcium concentrations relative to the surface waters. Pore Fluid I and the stream associated with it are enriched in calcium, but the pore fluid is enriched in chloride relative to the stream. Pore

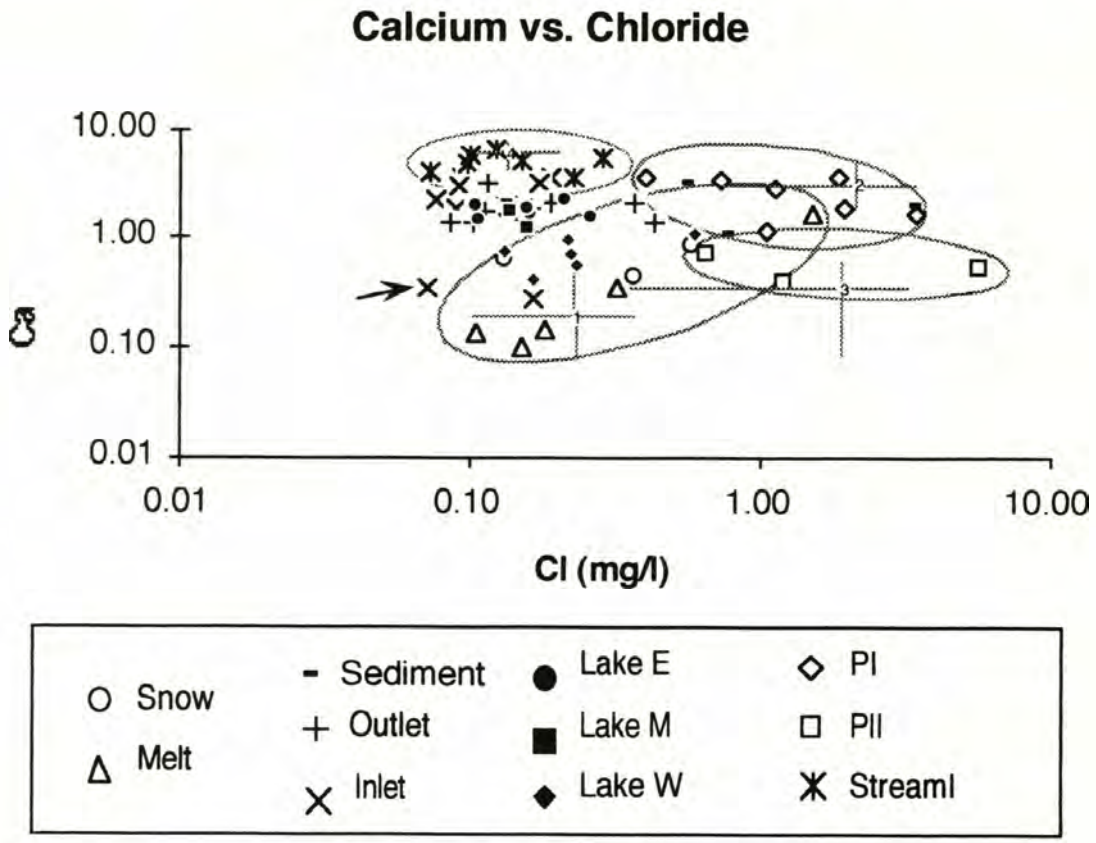


Figure 23: Mixing diagram for chloride and calcium. The numbers mark averages for mixing end-member clusters: 1) snow & melt, 2) Pore Fluid I, 3) Pore Fluid II, 4) Stream I. The average for Pore Fluid II includes two data points with calcium concentrations less than 0.01 mg/l, causing the average to appear low relative to the data shown on the plot. The data point indicated by an arrow was collected during a rainstorm.

Fluid I is depleted in calcium relative to its associated stream, suggesting that the stream is in direct contact with more vegetation than the pore fluid is and is therefore able to leach more calcium. The three lake sediment data points plot in the same field as Pore Fluid I. Even if more data were available for the lake sediments, the end-member defined by these data may not be distinguishable from the Pore Fluid I end-member. The outlet, inlet, and lake solutions plot in the same area between the four end-members clusters. Inlet samples collected following periods of high rainfall tend to have low chloride concentrations. The sample indicated by an arrow in Figure 23 is dilute in calcium relative to other chloride samples. This sample, collected on June 20, may correspond with the accelerated melting of snow in response to rising air temperature.

Appendix 5 gives the statistical data for the end-member clusters. The averages for the end-members are labeled (1) through (4). Averages include all data for each end-member. Some data points have cation concentrations of less than 0.01 mg/l and do not plot on the mixing diagrams. This causes the average for some end-members, including the Pore Fluid II end-member in Figure 23, to appear to be low relative to the data shown on the diagram. The quadrangle formed by the average end-members does not fit all of the surface-water data; however, the range of data included in the clusters effectively bounds all of the surface-water data.

Figure 24 shows a mixing diagram for chloride and magnesium. The correlation coefficient for chloride and magnesium is 0.732, indicating a significant relationship between the two. The average end-members are again designated with Arabic numerals. Solutions for snow, melt, and Pore Fluid II are depleted in magnesium relative to the other solutions with the pore fluid end-member enriched in chloride relative to the snow end-member. Pore Fluid I has the greatest concentrations of chloride and magnesium. Stream I is the

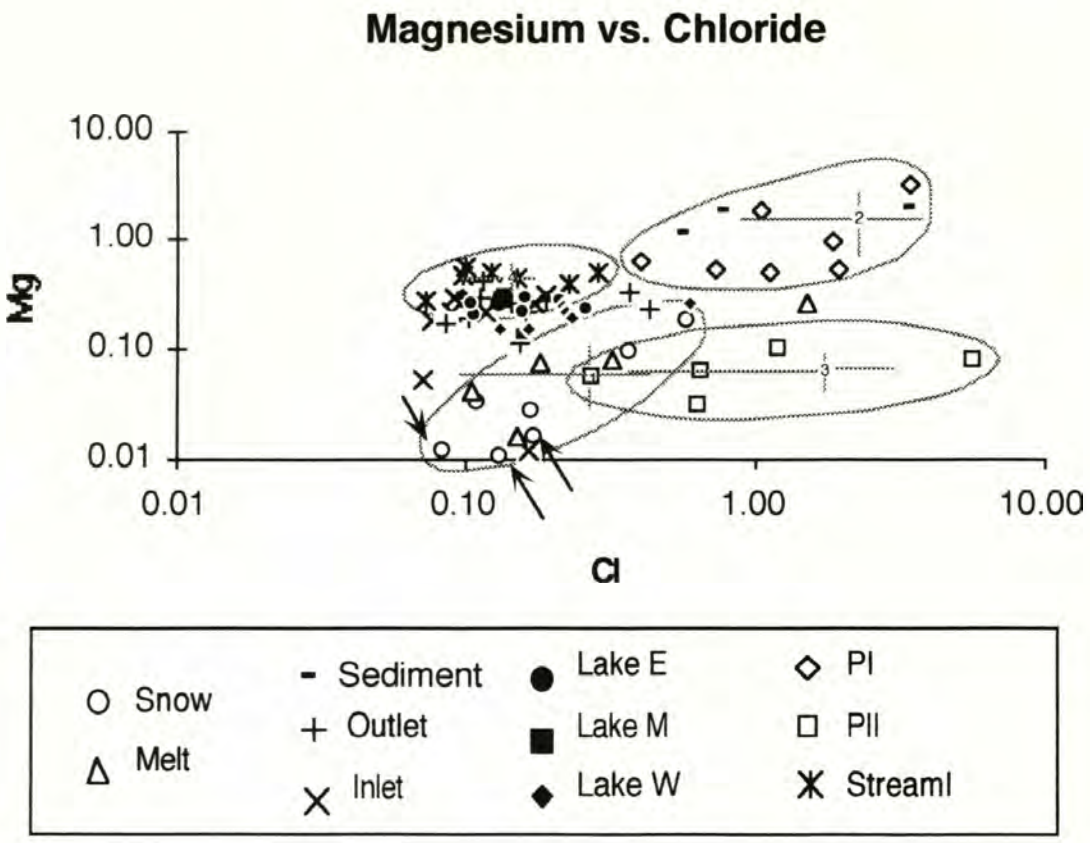


Figure 24: Mixing diagram for chloride and magnesium. Averages for mixing end-members are designated as 1 through 4. Data points from samples of new snow are indicated by arrows.

low chloride, moderate magnesium end-member. The surface-water samples fit well within the individual end-member clusters. The outlying inlet sample corresponds to the data point in Figure 23 that was attributed to rapid snowmelt. The snow samples indicated on Figure 24 are new snow samples collected in the early spring and late fall. A polygon based on this cluster of snow samples alone would contain more surface-water samples than the current configuration.

The mixing diagram for chloride and sodium (Figure 25) differs from the diagrams for calcium and magnesium in that the Stream I end-member cluster plots inside the surface-water cluster. A hypothesis for the reduced sodium of

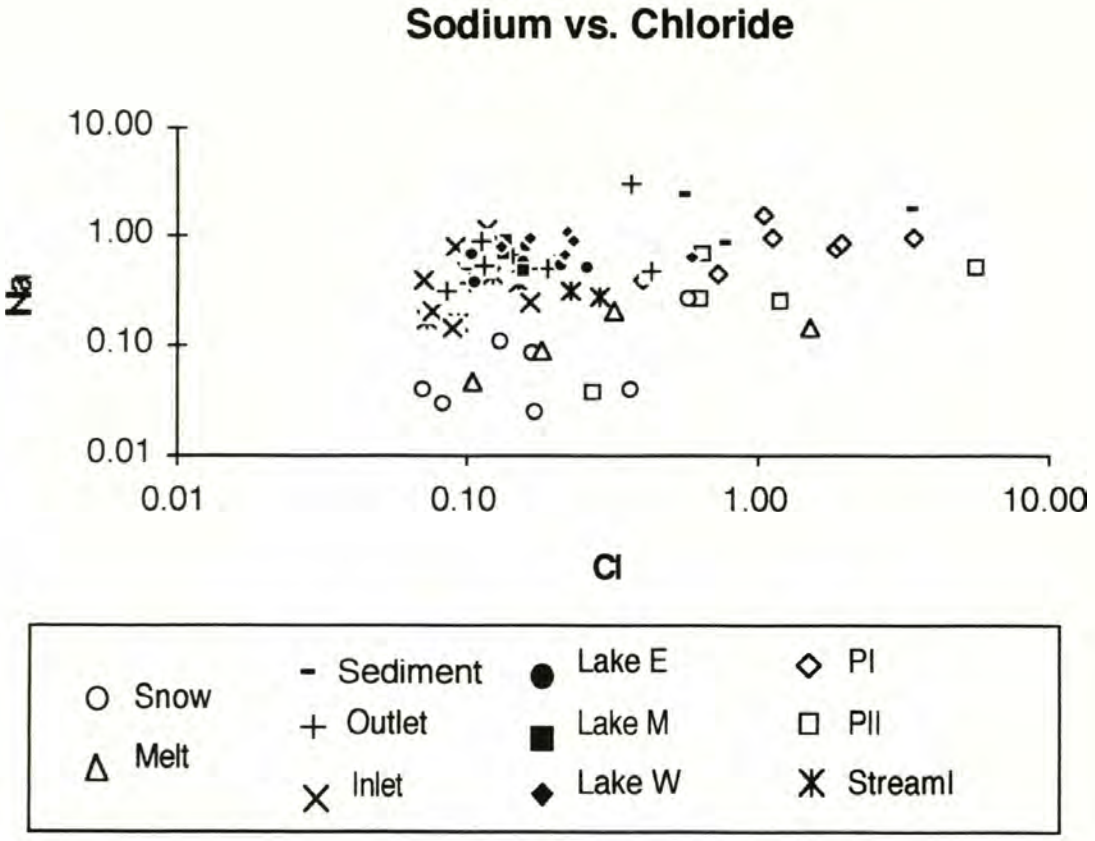


Figure 25: Mixing diagram for chloride and sodium.

the Stream I cluster is that less sodium is leachable from the vegetation relative to other major ions (Figure 22). The fact that Soil I acts as a high ion, low chloride end-member for calcium and magnesium may be more of a function of vegetation than soil chemistry. The correlation coefficient for chloride and sodium is 0.363, indicating that there is a significant correlation. The plot for Figure 25 is more scattered than that for Figure 24, reflecting the lower correlation coefficient.

The correlation coefficient for chloride and sulfate is 0.371, indicating a significant correlation. The configuration of the end-member clusters for sulfate (Figure 26) is similar to Figure 23. The polygon defined by the averages for the end-members doesn't contain the majority of the surface-water data even

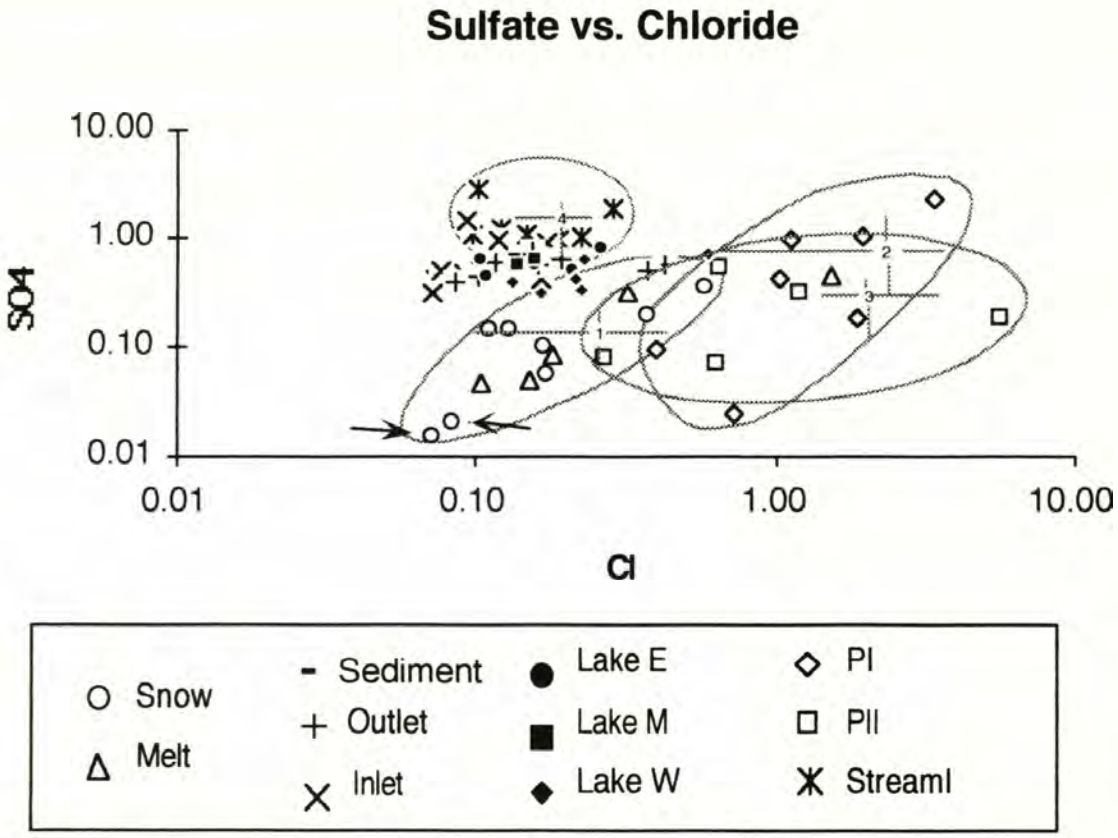


Figure 26: Mixing diagram for sulfate and chloride. The averages for mixing end-members are designated as 1 through 4. The data points indicated by arrows are from new snow samples.

though the end-member clusters surround the surface-water cluster. The snow data points with the lowest sulfate concentrations are from fresh snow.

The mixing diagrams for calcium, magnesium, and sulfate are moderately successful for showing surface waters as the mixing product of different end-members. The individual end-member clusters surround the surface water cluster.

In Figure 25, a high sodium, low chloride end-member has not been defined by the data collected in the field. The high sodium, low chloride end-member must be a solution that has a relatively low residence time, unlike Pore Fluid I or groundwater. A high residence time would result in a high chloride

end-member. Stream I itself has a low residence time relative to Pore Fluid I or ground water. The missing end-member may be a soil environment that has a very high permeability with ample vegetation contributing sodium. The vegetation must be leachable for sodium, unlike heather or grass. Huckleberry is a likely, although untested, candidate. The surface layer of soil may provide a rapid conduit for leached sodium to surface water bodies.

The snow and melt end-member is poorly defined. As discussed in previous sections, melt is enriched in most major ions relative to snow. Most of the data used for the low ion, low chloride end-member is derived from the snowfield, which has been enriched in most ions via wet and dry deposition of aerosols. Precipitation would provide a more valid low end-member for the mixing diagrams.

There are processes other than simple mixing that occur in a watershed. The mixing diagrams for nitrate (Figure 27A) and alkalinity (Figure 27B) plotted against chloride do not show evidence for the interaction between specific solutions. Both plots show a high degree of scatter. The correlation coefficient for chloride and nitrate is 0.024, indicating that there is not a correlation. Although the correlation coefficient for chloride and alkalinity is 0.614, suggesting a strong correlation, inspection of Figure 27B indicates that this is not the case. Most of the data are in a small cluster, with outliers that are not linear with the main cluster. Pearson's r is not valid for data sets such as alkalinity vs. chloride. The equilibria of nitrate and alkalinity are clearly controlled by processes other than mixing. Mixing diagrams for nitrate, and alkalinity do not provide evidence for the interaction of different fluids in the Upper Bagley watershed. The equilibria of these ions are more strongly impacted by biological activity or by gas exchange with the atmosphere. The equilibrium of nitrate is controlled by redox reactions coupled with biotic activity

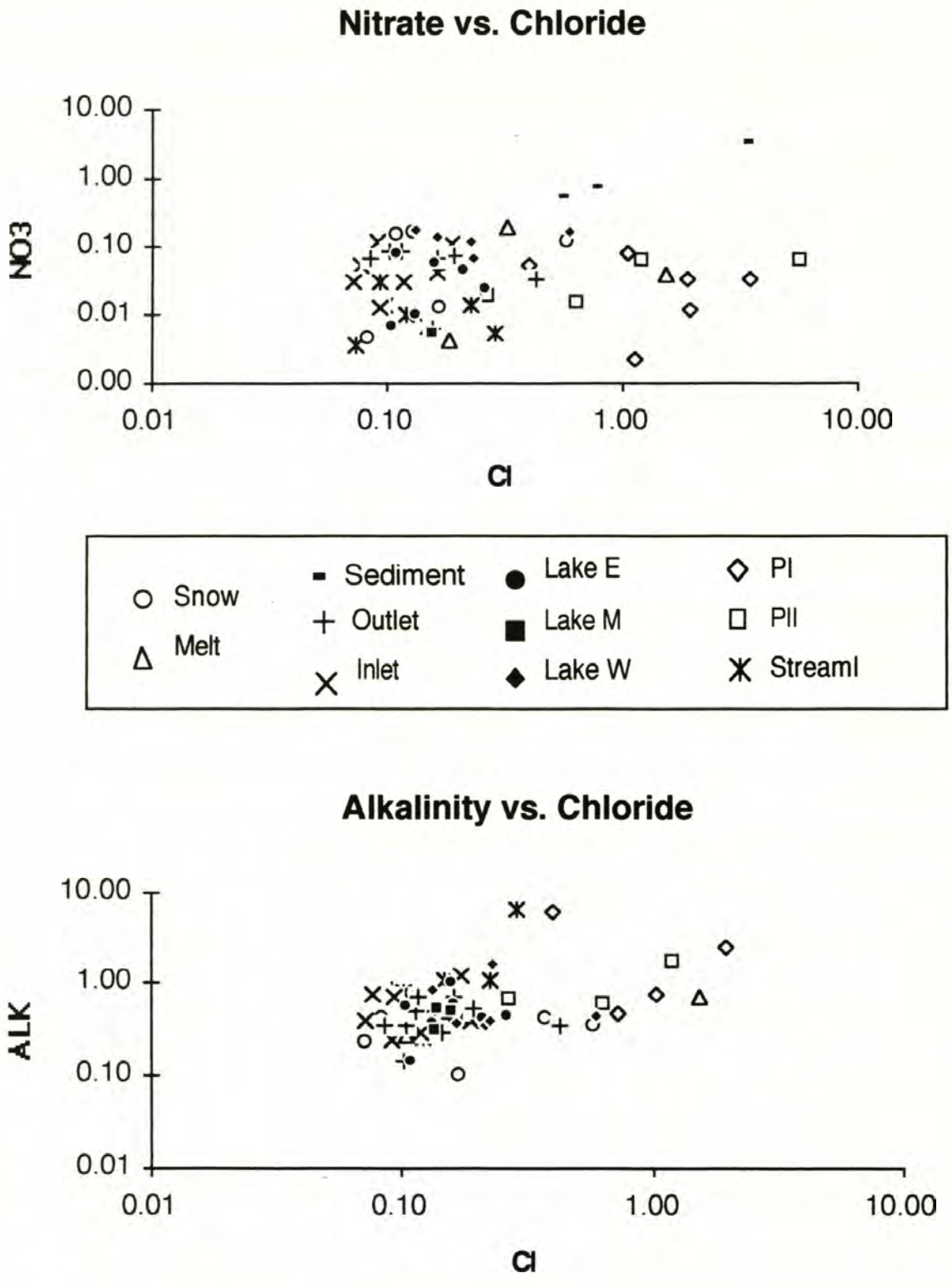


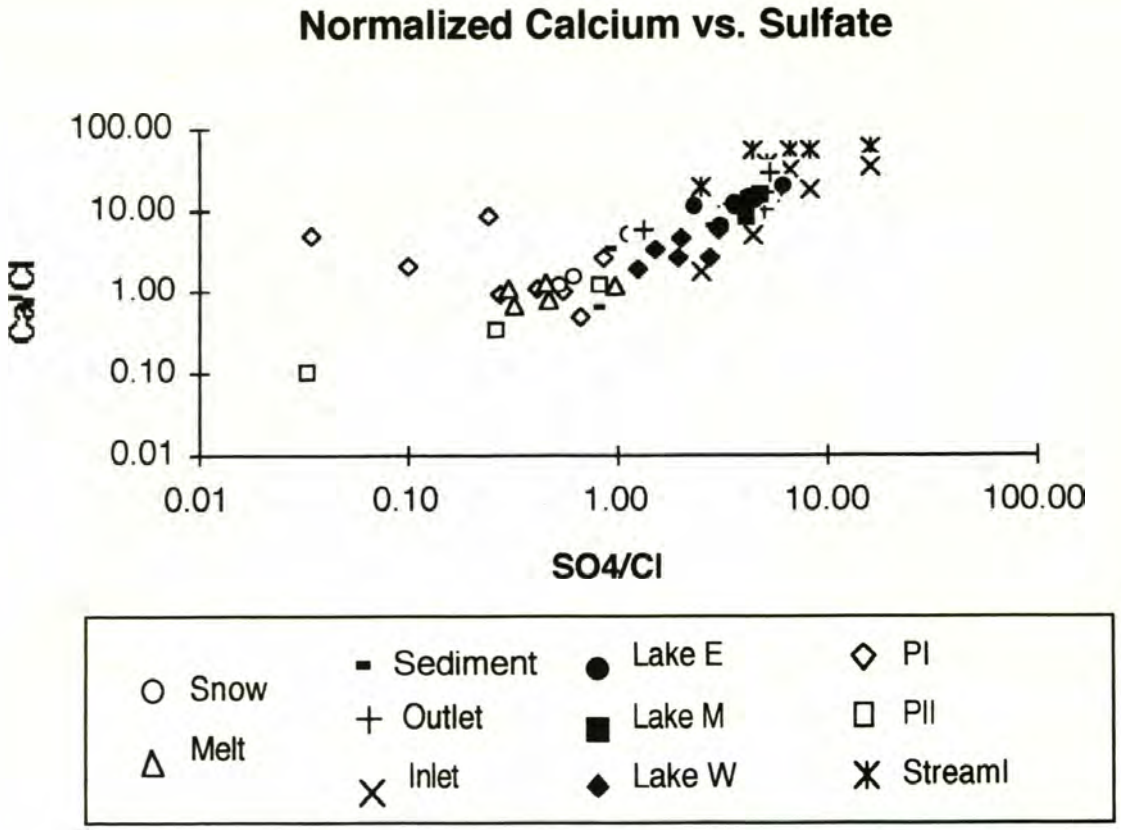
Figure 27: Mixing diagrams for nitrate (A) and alkalinity (B).

and gas exchange with the atmosphere. Alkalinity is controlled by gas exchange with the atmosphere.

A second approach, referred to here as normalized mixing analysis, is taken to describing the Upper Bagley watershed relative to mixing. Ions are normalized to chloride and are plotted on a log-log scale. Plots of normalized ions that demonstrated mixing using the EMMA approach form linear trends. Normalized mixing diagrams are useful for identifying data groups that diverge from ideal mixing. Once identified, the diverging data can be further interpreted to determine what processes influenced the chemical equilibrium of a solution or series of solutions.

Normalized calcium plotted against normalized sulfate shows a positive correlation with the pore fluid, snow, and melt clustered together (Figure 28A). Concentrations for calcium and sulfate are nearly equal to the concentration of chloride in this cluster. The pore fluids plot in this area because a relatively long residence time concentrates all three ions in solution. Snow and melt plot in this area because all three ions are present in low concentrations. Stream I plots at the distal end of the linear trend formed by the normalized mixing plot. Both calcium and sulfate are concentrated in Stream I relative to chloride, indicating that the solution leached calcium and sulfate but has a relatively short residence time in the vicinity of the ion source.

Three data points from Pore Fluid I diverge from the linear plot. These points correspond with the August sampling dates. These points also diverge in the normalized mixing diagram for magnesium and sulfate (Figure 28B). The process causing the divergence is the leaching of calcium and magnesium under acidic conditions, increasing the concentration of the cations in solution.



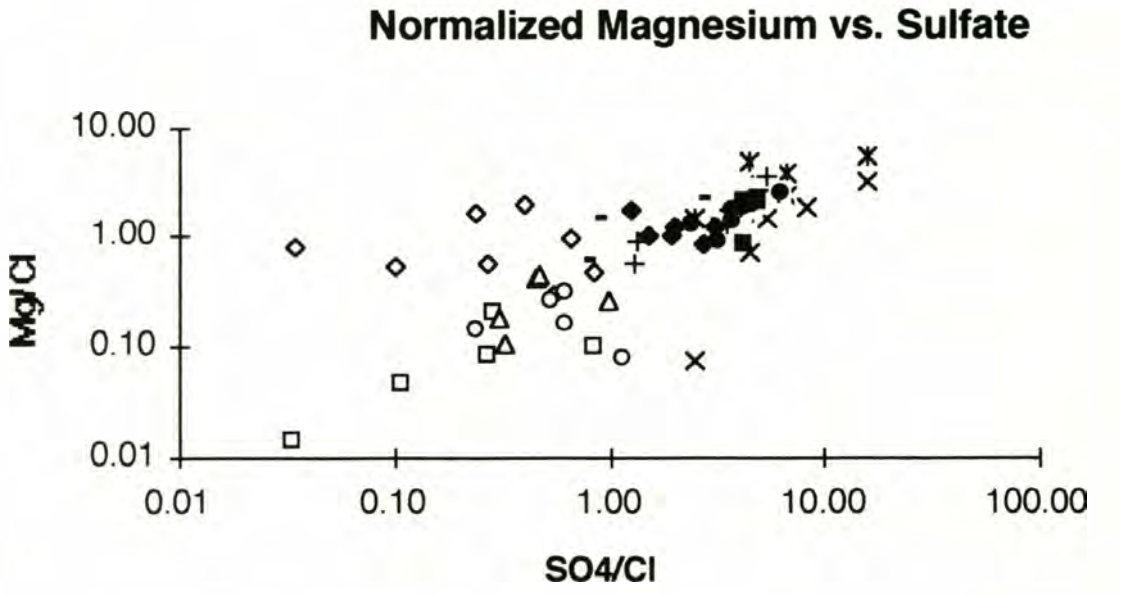


Figure 28: Normalized mixing diagrams for calcium vs. sulfate (A) and magnesium vs. sulfate (B).

The increased acidity of the soil solution is linked with the lack of rain preceding all three sampling dates. Acidic byproducts of microbial activity probably became concentrated until storm-flow water flushed the soils on August 2 and again on September 8. The samples, collected two weeks apart, provide an incomplete record of geochemical fluctuations in the Upper Bagley watershed.

Magnesium also diverges independently of calcium (Figure 28B). There is no correlation between divergent data points and precipitation pattern. Fluctuations in magnesium relative to chloride may reflect fluctuations in magnesium deposited in the watershed as an aerosol.

IV. CONCLUSIONS

The Upper Bagley watershed is described in this study as a set of three chemically distinct subsystems: 1) snowpack, 2) soil solutions, and 3) surface water, including the lake, the inlet, and the outlet. The snow, surface water, and pore fluids of the Upper Bagley watershed undergo chemical changes that are brought about by fluctuations in temperature, precipitation, and biological activity.

Snowpack

Melt water is enriched in calcium, magnesium, sodium, chloride, and sulfate relative to the ice it is derived from. Calcium and sodium concentrations are as much as three times greater in the melt fraction than in the snow fraction. The melt is enriched in magnesium by a factor of six relative to the snow late in the growing season. Chloride and sulfate concentrations are up to four times greater in the melt fraction. The increased concentration in the melt fraction is attributed to the accumulation of ions at the surface of ice crystals in the snowpack (Johannessen & Henriksen, 1978). Variations in the enrichment of ions in the melt relative to the ice are caused by fluctuating rates of melting in response to temperature and precipitation fluxes.

The distribution coefficient for alkalinity and nitrate is close to one. This suggests that water-ice interaction does not effect the concentration of either. Alkalinity is controlled by the interaction of the ice surface with CO_2 in the atmosphere. Nitrate is controlled in part by denitrification, the bacterial transformation of nitrate to nitrite.

Pore Fluids

Pore fluids extracted from the two soil types identified in the Upper Bagley watershed are chemically distinct from each other. Pore Fluid I is from a clay loam that is composed of montmorillonite, inorganic colloids, and organic acids. Pore Fluid II is from a gravely sandy loam derived from andesite and has a composition dominated by andesine and inorganic colloids. Because of the reaction sites provided by the clay and organic molecules, Pore Fluid I tends to have greater ion concentrations than Pore Fluid II. Pore Fluid I has a lower pH than Pore Fluid II. Laboratory modeling of the interaction between soil and water produced a Pore Fluid I enriched in sulfate and calcium by a factor of ten relative to Pore Fluid II. Nitrate was also present in greater concentrations in the Pore Fluid I.

The calcium concentration in Pore Fluid I increases in the middle of the growing season, peaking in early August before declining. The peak itself is an artifact of discrete sampling events that provide an incomplete record of geochemical cycles. Variations in calcium are attributed to acid conditions during periods of low soil moisture, increasing the amount of calcium leached into solution.

Pore Fluid I has detectable concentrations of potassium in early spring and in late fall. The potassium is attributed to the leaching of decaying vegetation by melt-water and precipitation.

Surface Water

The chemical composition of surface water in the Upper Bagley basin reflects the mixing of fluids derived from snow and soil solutions. Based on calcium, magnesium, and sulfate concentrations, the fluids from the inlet, outlet, and lake lie between four end-members 1) snow and melt 2) Pore Fluid I, 3)

Pore Fluid II, and 4) Stream I. The snow and ice end-member is not the most representative data set to use in defining the low concentration end-member of mixing because the data were taken primarily from the snowfield, which is chemically altered through water-ice interactions and through the deposition of aerosols. Stream I fails to act as an end-member for the mixing diagram for sodium. Stream I has high ion concentrations with low chloride concentrations suggesting that the fluid has a short residence time. The probable source of most ions is vegetation leachates. A plant leachate that has high sodium concentrations was not identified

Nitrate and alkalinity concentrations for the fluids do not provide evidence for interaction between fluids in the Upper Bagley watershed. The equilibria of these ions are more strongly impacted by biological transformations and gas exchange with the atmosphere.

Normalized mixing diagrams give evidence for processes other than simple mixing that influence chemical equilibria in the Upper Bagley watershed. Fluctuations in biotic activity, precipitation, and deposition of aerosols can overprint evidence for the mixing in watersheds.

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Appendix 1

Upper Bagley Lake Sampling Schedule, 1992

	4-Apr	13-May	21-Jun	5-Jul	20-Jul	2-Aug	16-Aug	30-Aug	27-Sep	25-Oct	29-Nov
Inlet			x	x	x	x	x	x	x	x	
Lake: East				x	x	x	x	x	x	x	
Middle						x	x	x			
West					x	x	x	x	x	x	
Outlet	x	x	x	x	x	x	x	x	x	x	x
Pore Fluid I			x	x	x	x	x	x	x	x	
Stream I			x	x	x	x	x	x	x	x	
Pore Fluid II					x	x	x	x	x		
Snow			x	x	x	x	x	x	x	x	
Snow Profile	x	x									
Melt					x	x	x	x	x		
Sediment					x		x		x		

Appendix 2

Chemical Data from Field Samples*

Date	Sample	Field pH	Lab pH	Ca	Mg	Na	K	Fe	Cl	NO3	SO4	Alk
4/4/92	Outlet	6.90	7.23	1.42	0.23	0.47	0.26	0.00	0.43	0.03	0.55	0.35
4/4/92	Snow 0		6.57	0.00	0.03	0.00	0.11	0.00	0.16	0.13	0.15	0.29
4/4/92	Snow 0 (dup)		6.79	0.00	0.00	0.00	0.09	0.00	0.06	0.15	0.13	0.29
4/4/92	Snow 1		6.52	0.00	0.00	0.00	0.13	0.00	0.11	0.03	0.06	0.29
4/4/92	Snow 2		5.94	0.00	0.00	0.14	0.18	0.00	0.36	0.06	0.13	0.24
4/4/92	Snow 3		7.18	0.00	0.04	0.00	0.14	0.00	0.16	0.04	0.09	0.31
4/4/92	Snow 3.5		7.35	0.00	0.00	0.00	0.11	0.00	0.15	0.05	0.10	0.32
5/13/92	Outlet	7.56	7.79	2.11	0.33	2.95	1.65	0.00	0.37	0.00	0.49	
5/13/92	Snow 0		7.22	0.00	0.02	0.02	0.29	0.00	0.17	0.05	0.05	
5/13/92	Snow 1		6.39	0.00	0.01	0.02	0.02	0.00	0.12	0.04	0.07	
5/13/92	Snow 1.5		6.20	0.00	0.06	0.23	0.50	0.00	0.61	0.04	0.15	
5/13/92	Snow 2		6.63	0.07	0.09	0.08	0.32	0.00	0.27	0.04	0.08	
6/21/92	Inlet	7.56	7.69	2.30	0.18	0.21	0.00	0.00	0.08	0.05	0.51	0.76
6/21/92	Outlet	8.04	7.22	1.39	0.18	0.32	0.00	0.00	0.09	0.07	0.39	0.34
6/21/92	P I			6.88	3.96	1.77	3.90	0.00	7.31	0.05	1.96	
6/21/92	Stream I	7.46		3.97	0.28	0.17	0.00	0.00	0.07	0.00	0.42	
6/21/92	Snow 0		7.57	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.31
6/21/92	Snow 0 (dup)		7.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.32
7/5/92	Inlet	8.44	6.91	1.87	0.22	0.14	0.00	0.00	0.09	0.11	0.48	0.24
7/5/92	Lake E		7.20	1.51	0.20	0.38	0.00	0.00	0.11	0.08	0.45	0.14
7/5/92	Outlet		7.29	1.42	0.20	0.38	0.00	0.00	0.10	0.08	0.45	0.14
7/5/92	P I		7.25	1.67	3.20	0.97	0.00	0.00	3.44	0.03	2.25	

Date	Sample	Field pH	Lab pH	Ca	Mg	Na	K	Fe	Cl	NO3	SO4	Alk
7/5/92	Stream I	7.13	7.08	3.58	0.27	0.16	0.00	0.00	0.09	0.03	0.50	0.25
7/5/92	Snow		7.30	0.00	0.03	0.08	0.00	0.00	0.17	0.01	0.10	0.10
7/20/92	Inlet	8.06	8.39	0.36	0.05	0.40	0.00	0.00	0.07	0.04	0.32	0.44
7/20/92	Inlet (dup)		7.19	0.36	0.05	0.40	0.00	0.00	0.07	0.02	0.31	0.36
7/20/92	Lake E	8.35	6.13	2.00	0.25	0.68	0.00	0.00	0.10	0.01	0.64	0.56
7/20/92	Lake W	8.31	6.63	0.43	0.16	0.98	0.00	0.00	0.16	0.14	0.31	0.35
7/20/92	Outlet	8.40	6.19	2.00	0.26	0.70	0.00	0.00	0.10	0.00	0.62	0.35
7/20/92	P I	6.01	6.15	2.86	0.52	0.96	0.00	0.00	1.13	0.00	0.95	
7/20/92	PIb			1.43	0.27	0.96	0.00	0.00	2.13	0.00	0.71	
7/20/92	Stream I	7.80	6.36	5.00	0.47	0.43	0.00	0.00	0.10	0.01	1.10	0.84
7/20/92	P II		7.25	0.71	0.06	0.68	0.00	0.00	0.64	0.00	0.53	
7/20/92	Stream II	8.39	7.46	0.36	0.05	0.27	0.00	0.00	0.11	0.13	0.35	0.36
7/20/92	Snow		6.68	0.86	0.18	0.27	0.00	0.00	0.58	0.12	0.36	0.35
7/20/92	Melt	8.39	7.61	0.36	0.08	0.20	0.00	0.00	0.32	0.19	0.31	
8/2/92	Inlet	8.43	8.00	0.28	0.01	0.25	0.00	0.00	0.16	0.04	0.41	0.41
8/2/92	Lake E	7.80	7.04	1.56	0.24	0.50	0.00	0.00	0.26	0.02	0.81	0.45
8/2/92	Lake M	8.16	8.15	1.21	0.13	0.48	0.00	0.00	0.16	0.01	0.64	0.49
8/2/92	Lake W	8.18	7.48	1.09	0.27	0.62	0.00	0.00	0.59	0.16	0.73	0.41
8/2/92	Outlet	8.02	7.47	1.56	0.11	0.46	0.00	0.00	0.16	0.01	0.76	0.41
8/2/92	P I		6.42	3.50	0.63	0.40	0.00	0.34	0.40	0.05	0.10	5.66
8/2/92	Stream I	6.90	6.29	5.44	0.50	0.27	0.00	0.00	0.29	0.01	1.91	6.57
8/2/92	P II	8.83	8.08	0.00	0.06	0.04	0.00	0.00	0.27	0.02	0.08	0.67
8/2/92	Snow		7.56	0.44	0.10	0.04	0.00	0.00	0.37	0.00	0.20	0.41
8/2/92	Melt	8.58	7.77	1.62	0.26	0.14	0.00	0.00	1.52	0.04	0.46	0.69
8/2/92	Sediment			1.11	0.19	0.87	0.00	1.01	0.74	1.70	0.65	

Date	Sample	Field pH	Lab pH	Ca	Mg	Na	K	Fe	Cl	NO3	SO4	Alk
8/16/92	Inlet	7.20	6.36	1.99	0.22	1.18	0.00	0.00	0.12	0.03	0.96	0.30
8/16/92	Lake E	7.80	6.84	1.70	0.26	0.71	0.00	0.00	0.13	0.01	0.60	0.36
8/16/92	Lake M		7.47	1.99	0.28	0.70	0.00	0.00	0.13	0.00	0.64	0.31
8/16/92	Lake W	7.70	7.44	0.97	0.25	0.67	0.00	0.00	0.22	0.00	0.43	0.32
8/16/92	Outlet	7.80	7.15	1.77	0.26	0.70	0.00	0.00	0.14	0.00	0.59	0.30
8/16/92	P I		6.00	3.38	0.54	0.45	0.00	0.00	0.72	0.00	0.02	0.44
8/16/92	Stream I	7.20	6.03	6.38	0.51	0.44	0.00	0.00	0.12	0.01	1.26	0.26
8/16/92	P II		7.17	0.00	0.03	0.26	0.00	0.00	0.64	0.01	0.07	0.59
8/16/92	Snow	7.30	7.35	0.00	0.00	0.04	0.00	0.00	0.07	0.00	0.02	0.23
8/16/92	Melt		7.07	0.16	0.08	0.06	0.00	0.00	0.14	0.00	0.07	0.26
8/16/92	Melt (dup)		7.07	0.00	0.00	0.03	0.00	0.00	0.07	0.00	0.02	
8/30/92	Inlet	6.70	6.36	3.01	0.29	0.79	0.00	0.00	0.09	0.01	1.46	0.71
8/30/92	Lake E	7.30	6.84	1.68	0.29	0.83	0.00	0.00	0.16	0.00	0.59	0.62
8/30/92	Lake M	7.30	7.47	1.77	0.29	0.90	0.00	0.00	0.14	0.00	0.58	0.55
8/30/92	Lake W	6.80	7.44	0.72	0.22	1.07	0.00	0.00	0.22	0.12	0.34	0.36
8/30/92	Outlet	7.70	7.15	1.77	0.30	0.89	0.00	0.00	0.11	0.00	0.55	0.52
8/30/92	P I		6.00	3.69	0.97	0.77	0.00	0.00	1.87	0.03	0.19	
8/30/92	Stream I	6.60	6.03	5.74	0.57	0.48	0.00	0.00	0.10	0.00	2.83	0.81
8/30/92	P II		7.17	0.53	0.08	0.50	1.38	0.00	5.64	0.06	0.19	
8/30/92	Snow		7.35	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.02	0.37
8/30/92	Melt	5.70	7.07	0.10	0.02	0.00	0.00	0.00	0.15	0.00	0.05	0.37
8/30/92	Sediment			3.26	1.16	2.37	2.43	0.00	0.54	0.09	1.39	
9/27/92	Inlet	7.10	6.70	3.65	0.31	0.56	0.00	0.00	0.19	0.11	0.95	0.39
9/27/92	Lake E	7.10	6.69	2.37	0.27	0.53	0.00	0.00	0.20	0.05	0.37	0.37
9/27/92	Lake E (dup)	7.10	6.99	2.20	0.27	0.54	0.00	0.00	0.22	0.04	0.63	0.48

Date	Sample	Field pH	Lab pH	Ca	Mg	Na	K	Fe	Cl	NO3	SO4	Alk
9/27/92	Lake W	7.50	6.69	0.57	0.19	0.93	0.74	0.00	0.23	0.06	0.63	1.53
9/27/92	Outlet	7.20	7.45	2.11	0.27	0.51	0.00	0.00	0.19	0.07	0.62	0.55
9/27/92	P I		6.89	1.86	0.53	0.87	0.92	0.93	1.94	0.01	1.05	2.42
9/27/92	Stream I	7.20	6.40	5.20	0.44	0.38	0.00	0.00	0.15	0.01	1.08	1.11
9/27/92	P II		7.45	0.40	0.10	0.24	0.00	0.00	1.20	0.06	0.32	1.77
9/27/92	Snow		7.95	0.00	0.01	0.03	0.00	0.00	0.08	0.00	0.02	0.41
9/27/92	Melt		7.84	0.14	0.08	0.09	0.00	0.00	0.18	0.00	0.09	0.42
9/27/92	Lower Bagley	7.10	6.39	1.68	0.28	0.57	0.00	0.00	0.25	0.03	0.69	0.70
10/25/92	Inlet		7.35	3.13	0.27	0.52	0.00	0.00	0.17	0.07	0.91	1.26
10/25/92	Inlet (dup)		7.63	3.13	0.26	0.53	0.00	0.00	0.18	0.07	0.91	
10/25/92	Lake E		8.00	1.91	0.22	0.57	0.00	0.00	0.16	0.06	0.58	1.01
10/25/92	Lake W		7.68	0.75	0.15	0.82	0.00	0.00	0.13	0.17	0.40	0.82
10/25/92	Outlet		7.42	1.91	0.21	0.52	0.00	0.00	0.16	0.06	0.57	0.70
10/25/92	Outlet (dup)			1.91	0.21	0.52	0.00	0.00	0.17	0.06	0.57	
10/25/92	P I		5.64	1.15	1.92	1.55	0.87	>10	1.04	0.08	0.42	0.72
10/25/92	Stream I		6.43	3.70	0.40	0.32	0.00	0.00	0.23	0.01	1.02	1.10
10/25/92	Snow		7.95	0.62	0.01	0.11	0.00	0.00	0.13	0.16	0.15	0.43
10/25/92	Sediment			2.01	2.01	1.74	1.95	>10	3.29	0.02	2.54	
10/25/92	Lower Bagley		7.38	1.75	0.21	0.50	0.00	0.00	0.16	0.03	0.61	0.69
11/29/92	Outlet		7.35	3.27	0.33	0.00	0.56	0.00	0.11	0.07	0.59	0.66
11/29/92	Outlet (dup)		7.76	3.27	0.50	0.00	0.53	0.00	0.12	0.10	0.62	0.74

* Concentrations are in mg/l

Appendix 3

Soil Leachate Data*

PI	22-Jan	29-Jan	5-Feb	12-Feb	19-Feb	26-Feb	5-Mar
Ca	0	0.53	0.73	0.88	0.98	0.46	0.46
Mg	0	0.08	0.12	0.15	0.16	0.11	0.12
Na	0	0.10	0.12	0.14	0.14	0.11	0.10
K	0	0.00	0.00	0.00	0.00	0.00	0.00
Cl	0	0.13	0.13	0.13	0.12	0.08	0.11
NO_3	0	0.35	0.45	0.51	0.31	0.04	0.03
SO_4	0	0.49	0.73	0.94	0.99	0.73	0.71
PII	22-Jan	29-Jan	5-Feb	12-Feb	19-Feb	26-Feb	5-Mar
Ca	0	0.03	0.08	0.13	0.13	0.08	0.12
Mg	0	0.01	0.02	0.03	0.03	0.02	0.03
Na	0	0.02	0.03	0.03	0.08	0.05	0.05
K	0	0.00	0.00	0.00	0.00	0.00	0.00
Cl	0	0.09	0.12	0.08	0.21	0.05	0.06
NO_3	0	0.07	0.16	0.12	0.08	0.03	0.02
SO_4	0	0.02	0.05	0.05	0.06	0.05	0.06

* Concentrations are in mg/l

Appendix 4

Plant Leachate Data*

	Heather 1	Heather 2	Heather 3	Grass 1	Grass 2	Grass 3
Ca	0.13	0.00	0.00	0.16	0.46	0.50
Mg	0.04	0.05	0.02	0.26	0.50	0.50
Na	0.10	0.02	0.06	0.17	0.10	0.12
K	2.30	0.41	0.41	0.39	0.32	0.32
Cl	0.20	0.05	0.04	0.66	0.64	0.64
NO3	0.01	0.00	0.00	0.06	0.00	0.00
SO4	0.15	0.02	0.03	0.17	0.23	0.72
dry wt (g)	0.15	0.07	0.07	0.04	0.15	0.15

* Concentrations in mg/l.

Appendix 5

Statistics for Mixing Diagrams

	Ca			Cl		
	ave	St Dev	Conf.	ave	St Dev	Conf.
Melt/Snow	0.28	0.45	0.19	0.26	0.38	0.16
Stream I	4.88	1.02	0.60	0.14	0.08	0.04
PI	3.13	1.79	1.04	2.23	2.26	1.31
PII	0.33	0.32	0.24	1.68	2.24	1.65

	Mg			NO_3		
	ave	St Dev	Conf.	ave	St Dev	Conf.
Melt/Snow	0.06	0.08	0.03	0.05	0.07	0.03
Stream I	0.43	0.11	0.06	0.01	0.01	0.01
PI	1.53	1.36	0.79	0.03	0.03	0.02
PII	0.07	0.03	0.02	0.03	0.03	0.02

	Na			SO_4		
	ave	St Dev	Conf.	ave	St Dev	Conf.
Melt/Snow	0.07	0.08	0.03	0.13	0.14	0.06
Stream I	0.33	0.12	0.07	1.27	0.78	0.46
PI	0.97	0.48	0.28	0.87	0.85	0.59
PII	0.34	0.25	0.18	0.24	0.19	0.14

	ALK		
	ave	St.Dev	Conf.
Melt/Snow	0.36	0.14	0.06
Stream I	1.56	2.23	1.30
PI	2.31	2.40	1.39
PII	1.01	0.66	0.48

Concentrations are in mg/l.

$\alpha = 0.1$